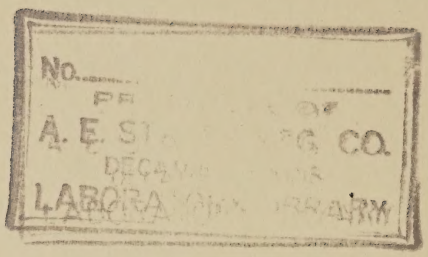

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Vol. XLIII.

1883. TRANSACTIONS.

LONDON:
J. VAN VOORST, 1, PATERNOSTER ROW.
1883.

1691

LONDON:
HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

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JOURNAL

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THE CHEMICAL SOCIETY.

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I.—*On the Constitution of some Bromine Derivatives of Naphthalene.* (Third Notice.)

By Raphael Meldola.

The present researches were undertaken with the object of extending my former work in the same field (*Ber.*, **11**, 1904, and **12**, 1861), and at the same time of contributing towards the clearing up of certain apparent inconsistences in the theory of the constitution of the dibromnaphthalenes.

By the direct action of 2 mols. of bromine on 1 mol. of naphthalene there is produced, as is well known, a mixture of several dibromnaphthalenes, distinguished by their different solubilities, crystalline forms, and melting points. On crystallising the mixed isomerides from alcohol, the first crystals deposited are those of the so-called β-dibromnaphthalene, which forms long transparent needles, melting at 81° C.

The mother-liquor on standing deposits a second crop of small white opaque needles, which Glaser (*Annalen*, **135**, 40) found to have a melting point of 76°; Jolin (*Bull. Soc. Chim.* [3], **28**, 514), in repeating this experiment, found the second crop of crystals (the so-called α-dibromnaphthalene) to have a melting point of 61°, and about the same time Guareschi (*Gazzetta*, 1877, 24) observed that Glaser's substance melting at 76° melted at 71° when impure. These statements embody our knowledge of the subject down to last year, when further experiments were undertaken by Magatti (*Gazzetta*, 1881, 357), who found that the second crop of crystals began to melt at 67°, but were not completely fused till 90°. The same range of melting point

was exhibited after several crystallisations from alcohol, but after crystallising from glacial acetic acid, a dibromnaphthalene crystallising in scales and melting at 120°, was isolated. After removal of the latter compound, which is identical with the γ-dibromnaphthalene of Jolin (*loc. cit.*) and of Darmstädter and Wichelhaus (*Annalen*, **152**, 298), the acetic acid solution deposited a crop of needles melting at 67—76°, and consisting of two, if not more, dibromnaphthalenes. The last communication on this subject is by Guareschi (*R. Accad. d. Sci. Torino*, **16**, 568), who has prepared a large quantity of the mixed dibromnaphthalenes by Glaser's method, and after separating the first crop of (81°) crystals, corrects the melting point (71°) of his former substance to 68°, and expresses the opinion that Glaser's substance melting at 76° was a mixture of the dibromnaphthalenes melting at 81° and 68°. As the result of the experiments of these different authors, it thus appears that by the action of bromine (2 mols.) upon naphthalene there are produced at least four dibromnaphthalenes, of which I am inclined to believe that the only two modifications as yet isolated in a state of purity, are the body melting at 81°, which crystallises from alcohol before any of the others, and the γ-modification separated by Magatti.

In 1879 (*Ber.*, **12**, 1961) I obtained a dibromnaphthylamine (m. p. 118—119°), from which, by the displacement of the NH_2-group by hydrogen, I prepared a dibromnaphthalene melting at 64°, and resembling in crystalline form the body melting at 81°. In order to see whether this dibromnaphthalene corresponded with any of the known modifications approaching it in its melting point, produced by the action of bromine on naphthalene, a quantity of the mixed isomerides was prepared in the usual way, and after removal of the modification melting at 81°, the crystals deposited by the mother-liquor were collected and re-dissolved in alcohol, and the solution was rapidly filtered as soon as crystals began to separate out. By this means I believe that every trace of the modification melting at 81° was removed, and the crystals deposited from the mother-liquor were collected and recrystallised from glacial acetic acid according to the method of Magatti. Rejecting the first fraction, which this author has shown to contain γ-dibromnaphthalene, the portion contained in the acetic acid solution was allowed to crystallise, and after another crystallisation from alcohol, it had a melting point of 68—70°. Equal weights of this purified substance and of my dibromnaphthalene melting at 64° were dissolved in equal quantities of alcohol and allowed to crystallise. The latter formed long transparent needles, resembling, as I have said, the modification melting at 81°, whilst the former crystallised in short mammellated tufts of opaque white needles. Now if the body melting at 68—70° is a definite isomeride, it is certainly

not identical with the modification melting at 64°, which I have given reasons for regarding as metadibromnaphthalene.*

Analysis of Metadibromnaphthalene.

A considerable quantity of this substance was prepared by the action of absolute alcohol upon the diazobromnaphthalene sulphate in the usual way, and was purified by several crystallisations from alcohol, with the addition of powdered animal charcoal.

0·5123 gram burnt with lime gave 0·670 gram AgBr.
Calculated for $C_{10}H_6Br_2$, 55·94 p. c. Br. Found, 55·66.

β-Dibromnaphthalene ($\alpha_1-\alpha_2$, m. p. 81°).

The constitution of this modification has been inferred with considerable certainty, and it has been shown to correspond with the β-dichlornaphthalene melting at 67—68°. The latter compound is obtained, amongst other processes, by the successive action of nitrous acid, hydrochloric acid, and PCl_5 upon amidonaphthalenesulphonic (naphthionic) acid; also by the action of PCl_5 upon bromnaphthalenesulphonic acid. The corresponding reactions with HBr and PBr_5 upon the same compounds furnish the dibromnaphthalene melting at 81°, which is thus inferred to have the two Br-atoms in the two α-positions in the same benzene-nucleus. Nevertheless, Guareschi (*Gazzetta*, **7**, 24) found that this dibromnaphthalene gave a bromphthalic acid melting at 135° on oxidation with nitric acid; and I also found that Jolin's nitro-dibromnaphthalene, when reduced and afterwards oxidised with nitric acid, gave the same bromphthalic acid. These results thus stand in contradiction to the generally received constitution of β-dibromnaphthalene. If the bromphthalic acid obtained by Guareschi and myself is a monobromo-compound, it is probably formed by a secondary reaction during the oxidation by nitric acid; or else we must believe that this dibromnaphthalene has one bromine-atom in each benzene-nucleus. Further experiments will be necessary to throw light on this question, and I propose to continue my investigation of the oxidation-products of Jolin's nitro-dibromnaphthalene with this object. In the meantime I have obtained β-dibromnaphthalene by a method which, to my mind, leaves little doubt as to the correctness of the generally received formula.

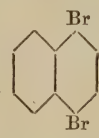
α-Acenaphthalide was brominated in acetic acid solution, and the bromacenaphthalide saponified by boiling for some time with strong caustic potash-solution. The bromnaphthylamine thus obtained, after

* *Loc. cit.*, p. 1693. A bromine determination came out somewhat low in the specimen of 68—70° m. p. substance above referred to.

crystallisation from dilute alcohol, was dissolved in strong sulphuric acid, the solution diluted with water, and the theoretical quantity of sodium nitrite necessary to form a diazo-compound was added in small portions to the well-cooled mixture. After removing an insoluble residue by filtration, bromine dissolved in glacial acetic acid was added to the filtrate as long as a precipitate formed. The diazo-perbromide formed a heavy orange-coloured amorphous precipitate, which was collected on a filter, well washed with cold water, and the water was finally displaced by glacial acetic acid. The perbromide was then transferred to a flask and warmed with glacial acetic acid on a water-bath as long as nitrogen was evolved. The solution, on cooling, deposited long white needle-shaped crystals, which were collected and purified by crystallisation from alcohol. This dibromnaphthalene melted at 81—82°, and on comparison proved to be identical with the β-modification produced by the direct action of bromine on naphthalene.

0·3442 gram burnt with lime gave 0·4523 gram AgBr.
Calculated for $C_{10}H_6Br_2$, 55·94 p. c. Br. Found, 55·92.

The bromnaphthylamine employed in this experiment is a para-compound, since it yields α-bromnaphthalene on displacing the NH_2 by hydrogen, and gives phthalic acid on oxidation (Rother, *Ber.*, **4**, 850). Thus the constitution of these bodies is—

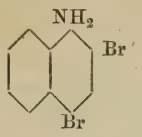


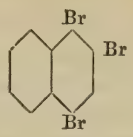
Tribromnaphthalene ($\alpha_1-\beta_1-\alpha_2$, m. p. 113—114°),

A quantity of the dibromacenaphthalide (m. p. 225°) prepared by the further action of bromine upon the monobrominated compound, was saponified by boiling with caustic potash, and the resulting dibromnaphthylamine melting at 118—119° was converted into a diazo-perbromide in the manner above described. The perbromide was thrown down as a yellow flocculent precipitate, and was decomposed by warming with glacial acetic acid in the usual way. Nothing separated out from the acetic acid solution when cold, but the addition of water caused the separation of minute white needles. These after several crystallisations from alcohol with animal charcoal were submitted to analysis:—

0·4925 gram burnt with lime gave 0·7558 gram $AgNO_3$.
Calculated for $C_{10}H_5Br_3$, 65·75 p. c. Br. Found, 65·31.

The constitution of this body and of the dibromnaphthylamine from which it is derived is thus:—





This tribromnaphthalene does not appear to agree in its properties with either of the three known modifications. It forms small white glistening needles easily soluble in ether, benzene, carbon disulphide, chloroform, and petroleum; less soluble in alcohol and acetone. The crystals separate out but slowly from alcohol even when the solution is nearly saturated at its boiling point and allowed to cool. The melting point is 113—114°.

Orthodibromnaphthalene (α_1—β_1, m. p. 63°).

The facility with which β-naphthylamine can now be prepared by the method of Merz and Weith (*Ber.*, **13**, 1298) has enabled several important additions to be made to our knowledge of the β-series of naphthalene-compounds. By brominating β-acenaphthalide in an acetic acid solution Cosiner (*Ber.*, **14**, 58) has recently obtained a monobrominated derivative, which has served me for the preparation of an eighth dibromnaphthalene. The following are the details of the experiment:—

β-naphthylamine was acetylated by cohobation with excess of glacial acetic acid, and the acetyl-compound purified by crystallisation from water. Brom-β-acenaphthalide was then prepared from this in the usual way, and after purification by crystallisation from alcohol, was converted by saponification into brom-β-naphthylamine. The latter compound was then converted into a dense yellow diazo-perbromide in the ordinary way, and the perbromide was heated with glacial acetic acid. The solution on cooling deposited a heavy oily substance, which after standing for some days solidified to a crystalline cake. The latter was dried by pressure between filter-paper in order to free it from a small quantity of an oily substance with which it was contaminated and purified by crystallisation from glacial acetic acid, and then from alcohol and animal charcoal. Many crystallisations were necessary before the dibromnaphthalene gave correct numbers on analysis, as the crystals which first separated out from the alcoholic solution were mixed with some substance containing a lower percentage of bromine (β-bromnaphthalene?).

I. 0·3678 gram burnt with lime gave 0·4840 gram AgBr.
II. 0·3311 „ „ „ 0·4350 „

		I.	II.
Calculated for $C_{10}H_6Br_2$, 55·94 p. c. Br.	Found..	55·99	55·91

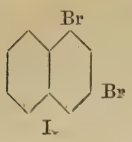
The melting point of this dibromnaphthalene is 63°, but although it approaches my meta-compound in this respect its crystalline form is perfectly distinct, not only from this, but from all the dibromnaphthalenes hitherto described. It crystallises in beautifully formed oblique rhombic prisms from alcohol, acetone, or petroleum, the latter solvent giving especially large and well-defined crystals. A strong alcoholic solution deposits the substance on cooling as an oil, which does not solidify for some time, so that in order to obtain crystals from this solvent it is better to dilute the alcohol with about 10 per cent. of water, and to crystallise slowly from a weak solution.

Constitution of the Dibromnaphthalene melting at 63°.—When one hydrogen-atom in a β-naphthalene-derivative is replaced by Br or NO_2 the α-position contiguous to the β-substituent appears to be attacked. This has been most clearly proved by the experiments of Jacobson (*Ber.*, **14**, 1791), who has shown that when β-acenaphthalide is nitrated an ortho-compound is produced, which by reduction gives a base free from oxygen. The monobrom-β-naphthol obtained by Smith (*Chem. Soc. Trans.*, **35**, 789)* has probably a similar constitution. It thus appeared extremely probable, *à priori*, that the new dibromnaphthalene and the bromnaphthylamine from which it is derived were ortho-compounds. That such is actually the case appears from the following experiments:—

(1.) Brom-β-naphthylamine was repeatedly evaporated on a water-bath with dilute nitric acid; a brittle resinous mass finally resulted, from which a large quantity of phthalic acid was obtained. The latter was identified by the melting point of its anhydride and by the fluoresceïn reaction. Thus *the bromine and* NH_2 *are in the same benzene-ring.*

(2.) Brom-β-naphthylamine was dissolved in a small quantity of sulphuric acid diluted with 10 per cent. of water, and the solution was further diluted and well cooled. A diazo-compound was formed by passing nitrous gas through the solution, and the latter was filtered into a large volume of absolute alcohol. After the decomposition of the diazobromnaphthalene and the removal of the excess of alcohol, &c., water caused the separation of an oily body having the boiling point and all the properties of α-bromnaphthalene. Thus *the bromine is in an α-position*, and the only formulæ possible are:—

* This brom-β-naphthol might furnish orthodibromnaphthalene by the action of PBr_5 but I have not yet tried this reaction.



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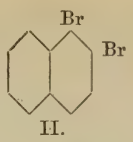
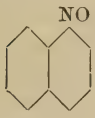
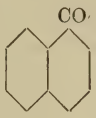
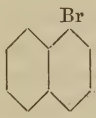


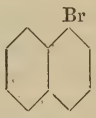
II.

The first formula is excluded by the fact that the new dibromnaphthalene is isomeric with the one described by me in 1879. The second formula must therefore be adopted, and the present dibromnaphthalene and Cosiner's brom-β-naphthylamine must be regarded as ortho-compounds belonging to the same series as β-naphthaquinone, nitroso-β-naphthol, &c.





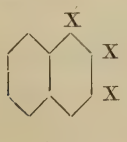




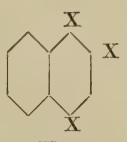
Orthodibromnaphthalene might be expected to occur among the low-melting products of the action of bromine upon naphthalene,* but I have not succeeded in detecting it in the so-called "α-dibromnaphthalene" (m. p. 68—70°) prepared for the purpose of comparison with metadibromnaphthalene. In order to see whether the crystalline form of orthodibromnaphthalene would be disguised by admixture with other isomerides, I made mixtures of this substance both with "α-dibromnaphthalene" (68—70°) and with metadibromnaphthalene, and crystallised from alcoholic solutions. In each case the microscope revealed the rhombic prisms of the ortho-compound amongst the needle-shaped crystals of the other modification.

Action of Bromine on Orthobromacenaphthalide.

Theory indicates the existence of two homonucleal† tri-derivatives of naphthalene, viz.:—



I.



II.

III.

* The low melting point (61°) of the α-dibromnaphthalene prepared by Jolin may have been due to the presence of this modification.

† For the sake of brevity, naphthalene derivatives having the substituents in the same benzene-nucleus may be called *homonucleal*, and those having the substituents in different benzene-nuclei may be termed *heteronucleal* derivatives. The simpler expressions, homo-derivatives and hetero-derivatives, do not meet the case, as they

II and III may be presumed to be identical, and it became interesting to see whether a second bromine-atom could be introduced into orthobrom-β-acenaphthalide. If this could have been effected, the resulting dibromacenaphthalide would have furnished on saponification a dibromnaphthylamine which by the elimination of the NH_2-group would have given either paradibromnaphthalene or the corresponding meta-compound. These arguments are of course based on the supposition that the second bromine-atom would enter the same nucleus as the other substituents. By a parity of reasoning, such a dibromnaphthylamine on replacing the NH_2 by Br might be expected to yield one of the tribromnaphthalenes of the above series, *i.e.*, either isomeric or identical with the tribromnaphthalene described by me in the former part of this paper. If identical, the α-position of the second bromine-atom would be demonstrated, and if isomeric, the β-position would be similarly proved. The same considerations obviously apply to the dibromnaphthalene obtainable from this dibromnaphthylamine.

By brominating orthobrom-β-acenaphthalide in an acetic acid solution, I have found, however, that the substitution is much more complex than that which gives rise simply to a dibrom-compound. One molecular proportion of the bromacenaphthalide was dissolved in glacial acetic acid, and one molecular proportion of bromine added to the solution. No absorption of bromine had taken place after standing for three days at the ordinary temperature, so the contents of the flask were warmed to about 70—80° for 24 hours, by which time the bromine had disappeared, and a white crystalline substance had separated out. The latter was purified by repeated crystallisation from alcohol, and a compound of constant melting point was at length isolated. This on analysis proved to be a tetrabromacenaphthalide :—

0·2939 gram burnt with lime gave 0·4429 gram AgBr.

Calculated for $C_{10}H_3Br_4.NH.C_2H_3O$, 63·87 p. c. Br. Found, 64·10.

The alcoholic mother-liquors appear to contain a complex mixture of bromine-derivatives from which nothing definite has as yet been isolated. The tetrabrom-compound forms very minute white needles melting at 138°. It is freely soluble in warm and but slightly soluble in cold alcohol; it dissolves in cold ether, acetone, chloroform, and benzene, and very freely in carbon disulphide. An experiment was made in order to obtain the corresponding tetrabromnaphthylamine, but three days' boiling with a syrupy solution of caustic potash failed to remove the C_2H_3O-group.

would indicate only dissimilarity of the substituents. It seems to be a very general law in the naphthalene series that homonucleal di-derivatives have lower melting points than their heteronucleal isomerides.

By brominating paranitracenaphthalide, I have obtained a brom-nitracenaphthalide crystallising in pale yellow needles, melting at 224—225°, and isomeric with the body obtained by Liebermann and Scheiding (*Ber.*, **8**, 1108) by nitrating parabromacenaphthalide, which melts at 232°. Experiments with a view to determine the constitution of this and of other nitrobrom-derivatives are in progress.

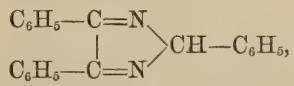
These researches have been conducted in the laboratory of the Atlas Works at Hackney Wick, and it gives me great pleasure to be able once again to record my obligations to Messrs. Brooke, Simpson, and Spiller.

II.—*On the Constitution of Lophine.* (Second Notice.)

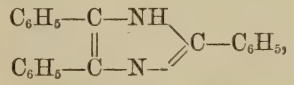
By Francis R. Japp, M.A., Ph.D., Assistant Professor of Chemistry in the Normal School of Science, South Kensington.

In No. 11 of the *Berichte*, 1882, p. 1493 (see also this Journal, 1882, Abstracts, p. 1063) Radziszewski communicates a new synthesis of lophine by the interaction of benzil, benzaldehyde, and ammonia. This reaction corresponds with the synthesis of para-hydroxylophine from benzil, parahydroxybenzaldehyde, and ammonia, described by Japp and Robinson (*Ber.*, 1882, p. 1268; this Journal, 1882, p. 326).

In discussing his synthesis, Radziszewski comes to the conclusion that lophine has the formula—



and rejects the formula—



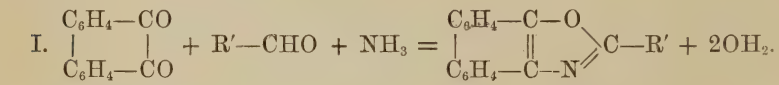
proposed by Mr. Robinson and myself.

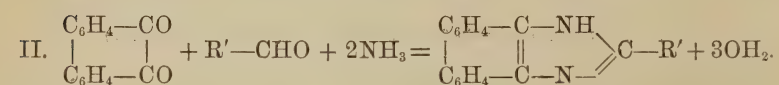
In the latter formula, lophine is represented as belonging to the class of the anhydro-bases described by Hübner. I shall, therefore, in the present paper, refer to this formula as the "anhydro-base formula" of lophine.

This formula was based chiefly upon certain analogies drawn from

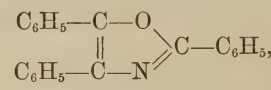
the reactions of phenanthraquinone with aldehydes and ammonia. I will now endeavour to show that these analogies are well founded, inasmuch as benzil really yields with aldehydes and ammonia the same classes of compounds as phenanthraquinone, though not always under the same conditions; further, that the anhydro-base formula explains the known reactions of lophine more consistently than that of Radziszewski; and lastly, I shall describe an experiment which, though not absolutely conclusive, affords a strong presumption in favour of the anhydro-base formula.

In order that what follows may be more readily understood, I will re-state here the two fundamental reactions of phenanthraquinone with aldehydes and ammonia:—





The first reaction occurs with non-hydroxylated, the second with hydroxylated aldehydes of the benzene series. This explains sufficiently why we resorted to the indirect method of employing a hydroxyaldehyde, and thus preparing first a hydroxylophine, instead of, like Radziszewski, acting upon benzil with benzaldehyde in presence of ammonia, and thus preparing lophine directly; for, following the analogy of the phenanthraquinone reactions, we must have expected in the latter case to obtain the compound—



by a reaction corresponding with that expressed in equation I.* In fact, previously to the publication of Radziszewski's paper, we had tried the reaction which he describes. We hoped to obtain the above oxygenated compound, and were surprised to find that the reaction yielded lophine. We conducted the experiment under conditions somewhat different from those adhered to by Radziszewski: instead of saturating an alcoholic solution of benzil and benzaldehyde with ammonia at a temperature of 40—50°, we heated molecular proportions of benzil and benzaldehyde with aqueous ammonia under pressure—on one occasion at 100°, on the second at 150°. In the first

* We were the more justified in this expectation, inasmuch as chrysoquinone—also a double ketone—yields, with benzaldehyde and ammonia, benzenylamidochrysole.

case the yield of lophine was 46 per cent. of the theory; in the second 93 per cent. I have repeated Radziszewski's experiment, and had no difficulty in obtaining lophine, but cannot confirm his statement as to the almost theoretical yield. On the contrary, the yield was in my hands but small.

With regard to the above oxygenated compound which I hoped to obtain from benzil, benzaldehyde, and ammonia, it is in the highest degree probable that this compound has been known for a very long time, without, however, its true nature being recognised. (The existence of this compound has, as I shall endeavour to show presently, a distinct bearing upon the question of the constitution of lophine.) Zinin (*Annalen*, **34**, 190), by adding aqueous ammonia to a warm alcoholic solution of benzil, obtained a compound to which he assigned the formula $C_{42}H_{30}N_2O_2$, and to which the name *azobenzil* was afterwards given. Halving this formula, we arrive at $C_{21}H_{15}NO$, the formula of the compound sought for. Zinin draws attention to the simultaneous production of ethylic benzoate in the reaction, and remarks that the formation of azobenzil is accounted for by this fact, without, however, explaining more precisely in what way this is the case. The formation from benzil and ammonia of a compound of Zinin's formula corresponds to a reduction, and Zinin probably only meant that this reduction was accounted for by the simultaneous oxidation of a portion of the benzil to benzoic acid.

Zinin's reaction may, I think, be interpreted in the following manner:—In the first place, a portion of the benzil is decomposed in presence of alcohol and ammonia, with formation of ethylic benzoate and benzaldehyde:—

$$\begin{matrix} C_6H_5{-}CO \\ \quad | \\ C_6H_5{-}CO \end{matrix} + C_2H_6O = C_6H_5{-}COOC_2H_5 + C_6H_5{-}CHO.$$

The benzaldehyde then reacts with a second molecule of benzil and one molecule of ammonia, yielding azobenzil:—

$$\begin{matrix} C_6H_5{-}CO \\ \quad | \\ C_6H_5{-}CO \end{matrix} + C_6H_5{-}CHO + NH_3 = \begin{matrix} C_6H_5{-}C{-}O \\ \quad \| \quad \diagdown \\ C_6H_5{-}C{-}N \end{matrix} \!\!> C{-}C_6H_5 + 2OH_2,$$

Azobenzil.

the reaction taking place according to equation I of the phenanthraquinone series.

In order as far as possible to test the correctness of this supposition, and to ascertain the nature of this compound, a quantity of it was prepared by Zinin's method. Aqueous ammonia was added to a warm alcoholic solution of benzil till a precipitate was produced; this

was then left in contact with the liquid at a temperature of about 70° for ten hours. Instead, however, of crystallising the substance from alcohol, it was found advantageous to extract the white crystalline powder, which formed the product of the reaction, with boiling light petroleum, in which the azobenzil readily dissolved, but the other substances present were practically insoluble. The solution on cooling deposits the pure compound in groups of fine colourless prisms. By crystallisation from boiling alcohol, it was obtained in the very lustrous long thin needles described by Zinin. The fusing point, which is not given by Zinin, was found at 115°. The substance boils above the range of the mercurial thermometer. A small quantity was boiled for some time in a test-tube without suffering the slightest decomposition—a behaviour which scarcely points to a compound containing 42 atoms of carbon in its molecule. Concentrated hydrochloric acid converts it into a gummy hydrochloride. Heated under pressure with the acid to 250°, it yields benzoic acid, ammonium chloride, and a resinous mass.

Analysis confirmed Zinin's results:—

	Substance.	CO_2.	OH_2.
I	0·1157	0·3607	0·0547

II. 0·1572 gram burnt with copper oxide in a vacuum gave 6·6 c.c. moist nitrogen at 22° and under 754 mm. pressure.

	Calculated for $C_{21}H_{15}NO$.		Found.	
			I.	II.
C_{21}	252	84·85	85·02	—
H_{15}	15	5·05	5·25	—
N	14	4·71	—	4·71
O	16	5·39	—	—
	297	100·00		

The vapour-density of the substance was determined by Victor Meyer's air-displacement method, heating in a lead-bath, with the following result:—

0·0881 gram displaced 7·3 c.c. air measured moist at 19°, and under 757·5 mm. pressure.

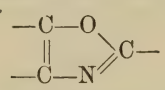
	Calculated for $C_{21}H_{15}NO$.	Found.
Vapour-density (air = 1)	10·28	10·23

The substance, therefore, possesses the formula and molecular weight here assigned to it, and the above may be regarded as the most probable account of the mechanism of the reaction in which it is formed.

If, on the other hand, in the reaction of benzil with ammonia, the benzaldehyde which is formed by the decomposition of 1 mol. of benzil were to react, together with *two* molecules of ammonia, upon a second molecule of benzil, lophine would be formed, the reaction taking place according to equation II of the phenanthraquinone series. In fact, Radziszewski has shown that lophine is obtained in small quantity by the action of ammonia upon benzil.

What I wish to point out is that in these cases—just as in the corresponding reactions between the methyl ether of salicylaldehyde, phenanthraquinone, and ammonia—we have the two reactions I and II taking place simultaneously with the formation of two compounds—one containing 1 atom, the other 2 atoms of nitrogen.

Now there is only one at all probable mode of formulating the compounds containing 1 atom of nitrogen, consistently with their formation from 1 mol. of double ketone, 1 of aldehyde, and 1 of ammonia. We must assume in them the existence of the complex of atoms—



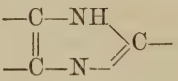
This is also in accordance with their decompositions. Thus benzenylamidophenanthrole and azobenzil, when heated with concentrated hydrochloric acid, are split up into benzoic acid and ammonia, whilst the phenanthrene and stilbene portions of the molecule are resinised under the conditions of the experiment.

We have therefore to assume that during the formation of the compounds containing 1 atom of nitrogen, an intramolecular re-arrangement occurs: the two carbon-atoms of the double ketone-group, —CO—CO—, become united by double bonds. This corresponds with what occurs when a quinone of the ortho-series—also a double ketone—is converted by the action of reducing agents into a quinol.*

* With phenanthraquinone, three cases of this intramolecular re-arrangement, occurring under the influence of reducing (or hydrogenating) agents, or of substances equivalent in their action to reducing agents, are known: the conversion of phenanthraquinone into phenanthraquinol by the direct addition of two atoms of hydrogen; the conversion of phenanthraquinone into the monethylic ether of phenanthraquinol, by the successive action of zinc-ethyl and water, the reduction in this case consisting in the indirect addition of the equivalent of two atoms of hydrogen in the shape of one atom of hydrogen and one ethyl-group; and lastly, the action of aldehydes, together with ammonia, upon phenanthraquinone. The formation of the double compound of phenanthraquinone with hydrogen sodium sulphite might perhaps be added to this list. Since in all such reactions the above-mentioned re-arrangement occurs in the carbon linkings of the closed lateral chain, no reactions in which phenomena of reduction are involved can be employed in determining the constitution of phenanthraquinone. Practically, all the arguments in favour of Graebe's formula for phenanthraquinone have been drawn from some such source. I hope

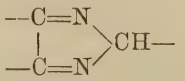
In the present case the reducing agent is an aldehyde, and, when the aldehyde has done its work, we have no longer an aldehyde-residue, but an acid-residue in the molecule of the new compound. The occurrence of this re-arrangement has been proved for three double ketones—phenanthraquinone, chrysoquinone, and benzil.

As regards the compounds containing 2 atoms of nitrogen in the molecule, it seems to me that the simplest way of formulating these is to assume in them the existence of the complex of atoms—



This is what I have done in the work on phenanthraquinone and in the paper on lophine published in conjunction with Mr. Robinson. I take for granted an intramolecular re-arrangement, such as occurs in the formation of the oxygenated compound.

Radziszewski, on the other hand, assumes in the latter class of compounds the existence of the complex—



Here the assumption of an intramolecular re-arrrangement is dispensed with, and this is so far a point in favour of Radziszewski's formula. This mode of formulating these compounds did not escape me; but I rejected it for the reasons above given. It seemed to me a more probable assumption that in two reactions of the same class—both condensations of double ketones with aldehydes and ammonia, both of the class of condensations in the ortho-series (employing the term "ortho" in an extended sense)—occurring simultaneously in the same operation, an intra-molecular re-arrangement which must occur in the one and which is conditioned by the reducing action of the aldehyde, should also occur in the other, the same condition being again present.

Up to this point I have described the grounds of analogy which led me to prefer the anhydro-base formula for lophine to that of Radziszewski. It now remains to regard the two formulæ from the point of view of the reactions of lophine.

Radziszewski finds a confirmation of his formula in the fact that lophine, when fused with potassium hydrate, yields benzyl alcohol and benzoic acid; and he ascribes the formation of these substances to the action of the alkali upon benzaldehyde furnished by the decomposition

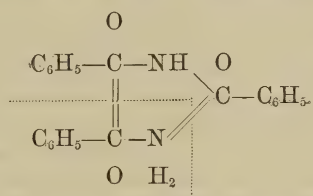
shortly to be able to lay before the Society an account of some reactions which are not open to the above objection, and which appear to me to decide in favour of Fittig's formula.

of the lophine. I cannot find that this reaction decides either way. A compound of the anhydro-base formula would split up under the influence of the alkali into benzoic acid, ammonia, and the hypothetical compound—

$$\begin{array}{c} C_6H_5\text{—}C(OH) \\ \| \\ C_6H_5\text{—}C(OH) \end{array}$$

a compound which corresponds with 2 mols. of benzaldehyde, and would be decomposed by the alkali with formation of the benzoic acid and benzyl alcohol obtained by Radziszewski.

By careful oxidation, lophine yields benzamide and dibenzamide, according to the equation: $C_{21}H_{16}N_2 + OH_2 + O_2 = C_6H_5.CO.NH_2 + NH(C_6H_5.CO)_2$ (Fischer and Troschke). If we adopt the anhydro-base formula, this reaction is readily accounted for. It is only necessary to assume that, as is usual in the oxidation of unsaturated compounds, the separation of the parts of the molecule occurs at the points where the atoms are connected by double bonds:—



It is difficult to see in what way Radziszewski's formula can account for this reaction.

One point in which the anhydro-base formula appeared to satisfy all requirements was the way in which it accounted for the formation of compounds containing alcohol-radicles; for example: Kühn's ammonium-compound, diethyl-lophinium iodide, $C_{21}H_{15}(C_2H_5)_2N_2I$ (cf. this Journal, Trans., 1882, 329), a compound corresponding with Hübner's diethylanhydrobenzdiamidobenzene iodide, $C_{13}H_9(C_2H_5)_2N_2I$. In Radziszewski's lophine formula there is no replaceable hydrogen-atom attached to nitrogen, so that the formation of this compound of Kühn's cannot be accounted for. Radziszewski perceives this difficulty, but I think that he underrates it. He says that the fact that lophine, although containing no hydrogen directly attached to nitrogen, yields compounds with alcohol-radicles "cannot surprise any one who has studied Hofmann's beautiful researches on the exhaustive action of methyl iodide upon conine and piperidine." The cases are, however, scarcely comparable. Dimethylconine and dimethylpiperidine were obtained by the *destructive distillation* of the corresponding ammonium-hydroxides—a process very different from that

employed in preparing diethyl-lophinium iodide, which Kühn obtained by heating lophine with ethyl iodide at 100°.

The following simple reaction appeared calculated to decide between the two formulæ. Radziszewski's formula contains, as already pointed out, a benzaldehyde-residue (benzylidene); the anhydro-base formula contains a benzoic acid-residue (benzenyl). Fischer and Troschke have shown that lophine may be heated with hydriodic acid and amorphous phosphorus to 220° without change. It seemed to me that if it were possible, by the action of the acid at a still higher temperature, to split up the lophine, a compound of Radziszewski's formula ought to yield benzaldehyde, which would then be reduced to toluene; whilst a compound of the anhydro-base formula would yield benzoic acid, which would not undergo further change. As benzoic acid could not, in presence of a powerful reducing agent like hydriodic acid, be furnished either by the dibenzyl-residue of Radziszewski's formula, or by the stilbene-residue of the anhydro-base formula, the formation of benzoic acid under these circumstances might be taken as deciding in favour of the latter formula.

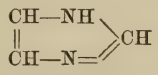
As a fact, I find that lophine when heated with hydriodic acid and amorphous phosphorus to a temperature a little over 300°, splits up, yielding benzoic acid. As the pressure with strong hydriodic acid proved unmanageable, a mixture of one volume of the strongest hydriodic acid with four volumes of fuming hydrochloric acid was employed instead. That a sufficiency of the reducing agent had been employed, was evident from the fact that, on cooling, the upper part of the tubes contained crystals of phosphonium iodide. The pressure on opening, in spite of the dilution with hydrochloric acid, was very great. The main portion of the lophine was recovered unchanged, the difficultly soluble lophine salt fusing together and thus escaping further action. No resinous products are formed.

Had the above reaction occurred at a lower temperature, I should have regarded it as absolutely conclusive against Radziszewski's formula. As it is, I think the probability that the benzoic acid can have been formed from anything else than a benzoic acid residue very slight. It is to be borne in mind that, as the temperature rises and the danger of bye-reactions increases, the power of the reducing agent also increases. Further, the temperature, though high, is at least 100° lower than that at which lophine boils without decomposition. According to a determination made by means of a Geissler high-temperature mercurial thermometer registering to 450° (with internal pressure to prevent the boiling of the mercury), lophine boils at 415° (uncorr.). Of course the indications of such an instrument areonly approximate.*

* Radziszewski also makes some highly ingenious suggestions concerning the con-

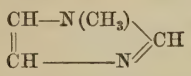
In fulfilment of the promise made in the former communication on the above subject, I have studied the action of other aldehydes, together with ammonia, upon benzil. Parahydroxybenzaldehyde yields,

stitution of glyoxaline, which he regards as "lophine, in which the three phenyl-groups are replaced by three hydrogen-atoms." He considers that when glyoxaline is formed by the action of ammonia upon glyoxal, a portion of the glyoxal first takes up the elements of water, yielding formic acid (the production of which in the reaction has been observed by Ljubavin) and formaldehyde; and that this last substance then reacts with glyoxal and ammonia to form glyoxaline, a reaction which would correspond with that in which lophine is formed from benzaldehyde, benzil, and ammonia. I do not at present propose to go into this subject further than to point out that if, while accepting the above analogy, we formulate glyoxaline on the basis of the anhydro-formula of lophine, thus :—

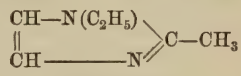


we arrive at a formula which, I consider, accounts better for the reactions of this compound than any of the formulæ which have as yet been proposed for it. The only fact connected with glyoxaline which this formula does not *readily* explain, is the identity of methylglyoxaline with oxalmethyline.

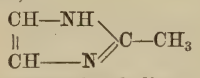
Addendum.—Since the above was written, Radziszewski has published a second paper (*Ber.*, **15**, 2706), in which he describes the synthesis of Wallach's paraoxalmethyline by the interaction of glyoxal, acetaldehyde, and ammonia—here again employing a reaction belonging to the class of condensations discovered by me. He does not appear to have expected to obtain paraoxalmethyline, but only *some* homologue of glyoxaline. He formulates paraoxalmethyline on the type of his lophine formula. I intend discussing this reaction more fully elsewhere, but in the meantime desire to take this opportunity of putting on record the following formulæ, which are founded upon the glyoxaline formula given above :—



Oxalmethyline
(identical with methylglyoxaline).



Oxalethyline.



Paraoxalmethyline.

These formulæ, which furnish a consistent account of the reactions of Wallach's oxalines, were constructed by me in August last, at which time I suggested to Dr. F. E. Matthews, who was then working with me, that he should attempt the synthesis of paraoxalmethyline from glyoxal, acetaldehyde, and ammonia. I thus predicted the result now obtained by Radziszewski. I wish, however, expressly to state that this train of thought was mainly suggested by the above speculations of Radziszewski on the formation of glyoxaline. But, at the same time, I do not think that it would have been possible for Radziszewski, holding the views which he does concerning the constitution of glyoxaline, to predict the formation of paraoxalmethyline in the above reaction.

as already described, parahydroxylophine. With salicylaldehyde a different reaction occurs: 2 mols. of aldehyde, together with 2 of ammonia, react with 1 of benzil, yielding a compound totally distinct in its properties from parahydroxylophine; thus:—

$$\underset{\text{Benzil.}}{C_{14}H_{10}O_2} + 2\underset{\text{Salicyl-aldehyde.}}{C_7H_6O_2} + 2NH_3 = \underset{\text{New compound.}}{C_{28}H_{24}N_2O_4} + 2OH_2.$$

Furfuraldehyde acts in a similar manner.

I hope to be able to lay before the Society, at an early date, the results of the investigation of this new class of compounds.

III.—CONTRIBUTIONS FROM THE JODRELL LABORATORY.

1.—*Contributions to the Chemistry of Lignification.*

By C. F. Cross and E. J. Bevan.

Following the views advanced by physiologists on the chemical phenomena of lignification, we were led to forsake the incrustation theory, as not adequately expressing the facts established concerning the origin, properties, and decompositions of the lignified substance, and to adopt, as a working hypothesis, the alternative view of lignose, or bastose, as we ventured to call the jute-fibre substance, viz., that it is a chemical whole in the sense of presenting a true combination rather than a mixture of cellulose with its non-cellulose constituents. Subsequent observations have further justified this course. By means of fractional solution in the ammonia-copper reagent, we uniformly obtained an amorphous modification of the fibre substance, exhibiting properties similar to the original as regards its behaviour both to chlorine and to acids.

In one particular, however, a difference is observed, in that the freshly precipitated amorphous modification gives only a slight reaction with aniline sulphate, and after a second solution and precipitation no coloration is obtained. That this reaction, supposed to be essentially characteristic of lignose, is in reality due to some product of change (probably of oxidation) is further shown by the fact that this property of giving a yellow colour with aniline salts is entirely lost after the substance has been boiled in a solution of sodium sulphite, the other properties remaining unaltered. We find moreover that a yellow reaction with aniline salts is characteristic of a number

of aromatic aldehydes. If, for instance, oil of cinnamon be shaken with a solution of the sulphate, the whole solidifies to a mass of bright yellow needles. Lignose we think, therefore, is to be considered apart from this property.

We have previously shown that jute is resolved in various ways, according to the methods or conditions brought to bear upon it, the cellulose for instance appearing either as cellulose or in the form of acids of the pectic class. So also the non-cellulose appears either as an astringent substance, or in the form of the chlorinated derivative previously described. In reference to the latter and its evident connection with the aromatic series, Dr. Armstrong directed our attention to the researches of Stenhouse and Groves on the chlorination of pyrogallol as probably bearing on the subject. We prepared mairogallol according to their method (*Chem. Soc. J.*, 1875), and found that both it and the amorphous substances which constitute the chief portion of the product give, when treated with sodium sulphite solution, a colour-reaction exactly resembling that which is characteristic of the freshly prepared lignose derivative. A close connection of these plant-constituents with the trihydric phenols, which can be seen to be suggested on grounds which are independent of this observation, we venture to think is thereby fairly established.

Following up this subject, we endeavoured to prepare a more highly chlorinated derivative of bastose. The derivative obtained by the action of chlorine gas upon bastose in presence of moisture is an amorphous yellow body, which, only when freshly prepared, gives the colour-reaction with sodium sulphite. Although this indicates the occurrence of molecular change during the process of purifying the body for analysis, and although its amorphous character places it in that much abused category of substances to which the ordinary criteria of purity are inapplicable, the numbers obtained in the analysis of preparations various in origin and differently prepared, were constant, and agreed with those required by the formula $n(C_{19}H_{18}Cl_4O_9)$. In justification of the adoption of this formula we would state first that it was our only guide in investigating the constitution of lignified fibres, and secondly, that substances which go to build up living tissues are of very necessity colloïds, and their immediate derivatives also; but because colloïds they are none the less definite, and at all events the method of ultimate analysis must be applied to their investigation until it is shown to be nugatory.

The chlorinated compounds experimented upon were obtained, the one from jute and the other from the fibre of *Musa paradisiaca*, a monocotyledonous plant. The purified fibres were exposed in the damp state to an atmosphere of chlorine gas, and the reaction being complete, the products were severally dissolved away by means of

alcohol, precipitated with water, washed and dried first in a vacuum, and lastly at 100°. These were then separately dissolved in glacial acetic acid, and further chlorinated after the manner described by Stenhouse and Groves. The products were separated by pouring the acetic solution into water, whereby they were precipitated in the form of a yellowish-white substance resembling wax. After washing and drying, first in a vacuum, and lastly at 100°, they were analysed, with the following results:—

(*a*). From jute. (*b*.) From Musa.

(*a*.) 0·4087 gave 0·5550 AgCl.
0·1234 „ 0·1788 CO_2 and 0·0435 H_2O.

(*b*.) 0·4892 „ 0·6689 AgCl + 0·0060 Ag.
0·1790 „ 0·2611 CO_2 and 0·0564 H_2O.

	(*a*.)	(*b*.)	Calc. $C_{38}H_{44}Cl_{11}O_{16}$.
C	39·52	39·77	40·0
H	3·92	3·50	3·8
Cl	33·50	34·20	34·0

The products are therefore identical. It is impossible to account for their derivation from the original tetrachlorobastin (which we may represent by the formula $C_{38}H_{36}Cl_8O_{18}$) by a symmetrical equation. At present we cannot do more than record the results as they stand.

Starting indeed with a highly complex molecule, such as both bastose and the lower chlorobastin certainly are, and in view of the further complicating action of chlorine upon the trihydric phenols and their derivatives, which has been established by the work previously cited, we have no reason to expect a resolution into simpler molecules by means of this reaction. It would appear that only in the absence of oxidising conditions can this be effected, and it is from this point of view that we are following up the resolution of bastose, lignose, and the chlorobastins by means of the sulphites under extreme conditions of temperature and pressure.

Note on the Constitution of Lignose.

We would record two recent observations which bear upon the question of the mode of union of the constituents of lignose. (1.) Dry chlorine has no action upon this substance, whereas the presence of moisture determines instant combination, with evolution of heat. (2.) The furfural-yielding constituent survives exposure to chlorine, the chlorinated jute fibre giving an abundant yield of this aldehyde by distilling with hydrochloric acid.

In conclusion, we wish to express to Sir Joseph Hooker and Professor Thiselton Dyer our recognition of the privilege of occupying the Jodrell Laboratory for the purpose of carrying out these researches, and our sincere thanks for their personal kindness to us during our stay.

Addenda.

(1.) *Note on the Sacchulmic Compounds.*

Sestini has recently published (*Gazzetta*, 1882, 292; *Chem. Soc. J.*, 1882, 1182) the results of an investigation of the action of the halogens upon the sacchulmic compounds, and we wish to call attention to the similarity of the products obtained by him to those which we have obtained from various substances of vegetable origin. For instance, the chloroxysacchulmide, $C_{22}H_{16}Cl_4O_{12}$, described by him is closely similar to the derivative obtained by chlorinating the black substance formed by the action of H_2SO_4 at 60—70° upon the carbohydrates, one preparation of which we analysed and found to be $C_{20}H_{16}Cl_4O_{10}$ (*Chem. Soc. J.*, **40**, 1122): these two derivatives are in their properties identical. The resinous matter obtained from the alkaline liquors from Esparto boilers yield a series of chloro-derivatives similar in composition and properties to the above; and generally the products of degradation of the carbohydrates, natural and artificial, yield chlorine substitution-products having similar characteristics. Should the presence of an aromatic group in these compounds, of which there appears to be some evidence (*Jahresb.*, 1871, 741; 1872, 771), be established, Sestini's results will throw additional light upon some of the difficult problems suggested by the changes which the carbohydrates undergo in plant tissues.

(2). Since reading this paper we have found that* Dr. Müller has preceded us in the observation that the reaction of aniline sulphate with lignified fibres, formerly supposed to be characteristic of lignose, is in reality due to some product of its change; this he succeeded in removing by means of *oxidising* agents, such as Schulze's solution, and dilute solution of chromic acid.

We do not appear to have been singular in overlooking this observation of Dr. Müller's, and we are glad to be able to reproduce it, and add the confirmation afforded by the observations in this paper.

* "Pflanzenfaser," foot-note to p. 11.

2.—*On the Oxidation of Cellulose.*

By C. F. Cross and E. J. Bevan.

On boiling cellulose with nitric acid (60 per cent.) it is slowly converted into oxalic acid. This decomposition may, however, by careful observation, be seen to take place in three stages. In the first place, the cellulose is thoroughly disintegrated, the change doubtless resulting in the formation of hydrocellulose (Girard, *Ber.*, **9**, 65). Oxidation of this into oxalic acid then ensues. A portion of the mass, however, yields but slowly to the action of the nitric acid, in consequence, as we find, of its conversion into an oxidised derivative, to which we have provisionally given the name *oxycellulose*. The quantity of oxycellulose produced appears to be about 30 per cent. of the cellulose acted upon. When thrown upon a filter and washed with hot water, the removal of the acid is attended with gelatinisation of the mass. In this state it is entirely soluble in dilute alkalis, and is precipitated from such solutions unchanged and in a form resembling pectic acid, on the addition of acids, as also of alcohol, saline solutions, or even strong solutions of the caustic alkalis. Observations of the composition of these precipitates showed that oxycellulose does not form compounds with bases, or at least only of a very weak order, the substance thrown down by alcohol or saline solutions retaining only traces of inorganic matter. Specimens of oxycellulose obtained from various sources and purified in different ways were analysed, after drying at 110°, with the following results:—

(*a.*) Prepared from cotton, dissolved in NaOH, precipitated with $BaCl_2$, and washed.

(*b.*) Prepared from jute, dissolved in NaOH, precipitated by HCl, and washed.

(*c.*) Prepared from jute, dissolved in NaOH, precipitated by HCl, and washed.

(*d.*) Prepared from pith of *Aralia papyrifera*, analysed directly after washing.

a. 0·1756 gram gave 0·2779 CO_2 and 0·0840 H_2O.
b. 0·1329 „ 0·2121 „ 0·0642 „
c. 0·1018 „ 0·1617 „ 0·0504 „
d. 0·1388 „ 0·2200 „ 0·0689 „

	a.	*b.*	*c.*	*d.*	Calc. for $C_{18}H_{26}O_{16}$.
C	43·16	43·52	43·32	43·23	43·40
* H	5·20	5·36	5·50	5·51	5·22
O	51·64	51·12	51·18	51·26	51 38

* Allowing for ash.

Oxycellulose dissolves in concentrated sulphuric acid with a pink colour; the dissolved body, when isolated, is found to be dextro-rotatory, and otherwise similar in properties to ordinary dextrin. The freshly-prepared oxycellulose is not coloured by iodine or by Schulze's solution, but the horny mass to which it dries is coloured deep blue by the latter. These facts, together with the formation of the "nitro"-body about to be described, establish the cellulosic character of oxycellulose. The "nitro"-body was prepared in the following way:—The gelatinous oxycellulose was washed with strong nitric acid until free from water, and was then diffused through a mixture of equal volumes of strong sulphuric and nitric acids, in which it quickly dissolved. The solution, after standing for about an hour, was poured in a fine stream into a large volume of water, by which the "nitro"-body was precipitated as a white flocculent mass. The product, after drying at 110°, was analysed according to Eder's method (*Ber.*, **13**, 169), with the following result:—*

0·2342 gram gave 25·20 c.c. NO at 770 mm. and 19·4° C.

Percentage of N.	Calc. for $C_{18}H_{23}O_{16}3(NO_2)$
6·48	6·63

Our object in studying this resolution is to contribute to the solution of the problem of the constitution of cellulose. The decompositions of cellulose, including the above, go to show that it is made up of a nucleus which exhibits considerable stability, and side groups which easily yield to oxidation, and whose removal appears to cause only a subsidiary change in the composition or properties of the original. We have commenced the study of the oxidation of cellulose, in presence of alkali, by means of permanganate; and in addition to products of low molecular weight, we have obtained a body exhibiting the characteristic properties of metapectic acid, a result which is in confirmation of the above hypothesis.†

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3. *The Analysis of Certain Plant Fibres.*

By C. S. Webster.

At the instance of Messrs. Cross and Bevan, I undertook the extension of the results obtained by them in the investigation of the jute fibre to a series of the more commonly occurring plant fibres, and the main results of this work are embodied in the following table:—

* We think it worthy of record that in a second determination by this method, with a larger quantity of substance (0·801 gram), when about 80 per cent. of the total NO had been expelled, the flask containing the boiling ferrous sulphate solution was shattered, with a violent explosion.

† Comp. H. Müller, "Pflanzenfaser," p. 15.

	Fibro-vascular bundles of monocotyledonous plants.					Bast fibres of dicotyledonous plants.					
	Agave Americana.	Yucca gloriosa.	Ananassa sativa (pine apple).	Musa Paradisiaca (Manilla).	Phormium tenax (New Zealand flax).	Boehmeria puya.	Urtica heterophylla (Nilgherry nettle).	Crotalaria juncea (Sunn).	Hibiscus strictus.	Linum usitatissimum (flax).	Corchorus capsularis (jute).
1. Yield of cellulose (Cl method)	81·2	80·8	76 3	62·8	86·3	83·8	95·0	76·9	63·0	82·0	75·0
2. Character of isolated cellulose	Fibres free.	Fibres free.	Fibres agglutinated.	Fibres agglutinated.	Fibres partially agglutinated.	Fibres partially agglutinated.	Fibres free.	Fibres free.	Fibres partially agglutinated.	Fibres free.	Fibres free.
3. Loss in boiling 1 p.c. HKO (5 minutes)	9·9	14·5	9·6	18·6	5·8	15·6	2·6	5·3	13·7	7·8	17·2
4. Ditto (60 minutes)	14·6	16·5	19·0	31·7	9·9	24·1	7·3	10·7	25·5	16·6	18·6
5. Ash.....	1·0	1·3	1·0	1·6	0·9	3·7	1·0	0·9	2·0	1·7	1·1
6. Aggregate elementary composition C	45·9	—	42·5	42·6	44·4	41·8	42·9	—	—	43·7	47·1
6. Aggregate elementary composition ..... H	6·1	—	5·6	5·6	5·9	6·0	5·9	—	—	5·9	5·9
7. Lignified or otherwise.....	Lignified.	Lignified.	Lignified.	Lignified.	Lignified.	Not lignified.	Not lignified.	Lignified.	Lignified.	Not lignified.	Lignified.

The specimens of fibres were obtained from the Museum at Kew Gardens.
Whole length samples were taken; purified by boiling in glacial acetic acid and afterwards in alcohol; dried at 100°.

The reactions of these fibres, which also form an essential feature in the diagnosis of their constitutions, are detailed below:—

Ammonio-copper Reagent.—These fibres without exception dissolve, more or less rapidly, in contact with metallic copper and strong ammonia. The conflicting impressions which prevail on this point are doubtless referable to the employment of this reagent in its several forms, and to the widely different activities of these.

Nitric Acid (in presence of sulphuric acid).

The substance of all the above fibres is converted by the action of the usual nitrating mixture into so-called nitro-derivatives, allied to the pyroxylins.

In the case of the lignified fibres, the reaction is accompanied by the development of a mahogany-red colour, which on washing gives place to the bright orange of the nitro-derivative in question.

Sulphuric Acid (conc.).—The fibres of *Boehmeria* and *Urtica* dissolve to colourless solutions, the solutions of the others are more or less dark coloured.

Chlorine Gas.—Chlorine substitution-derivatives are obtained from the fibre substance of the above fibres, with the exception of the *Boehmeria*, *Urtica*, and *Linum*, the derivatives giving in all cases the characteristic colour-reaction with sodium sulphite.

Aniline Sulphate.—The solution of this substance, as also of the soluble aniline colours, is a valuable aid in diagnosing the fibres in regard to the distribution of the lignification, and also of encrusting substances. Neither the *Boehmeria*, *Urtica*, nor *Linum* gives any reaction; the *Ananassa* is coloured a uniform faint greenish-yellow; the *Yucca* and *Agave* a pale gold; *Hibiscus* bright yellow and streaky; *Crotalaria* a pale yellow and streaky; and *Musa* a bright gold, also streaky.

Aniline Colours.—As is well known, the dyeing properties of the fibres vary with the lignification, and this appearing to be correlated with the development of phenols, we may hope to be able to arrive at a more correct understanding of this phenomenon.

In dyeing these fibres with a neutral solution of the so-called alkali blue, the effects appear to follow an inverse course, the *Boehmeria* showing the deepest colour, the lignified fibres being much paler. This fact is probably referable to the presence of "pectous" substances in the former, and the reaction may prove to be of general use in indicating the presence of acids or acid-forming substances in the plant tissues.

In conclusion, I would note the grounds upon which the several determinations included in this method of diagnosis are based:

(1.) The yield of cellulose is of sufficiently obvious value, and an observation of its characteristics (2) is the qualitative supplement.

The most important differences shown by the various celluloses are in relation to the solvent action of the alkalis upon them, and the degree of this action is usually shown by the condition of the cellulose fibres after washing and drying. The products of the action are in the first instance gelatinous, and those fibres which undergo degradation thereby, show an agglutination of the cellulose fibrils on drying. (3.) The loss of weight sustained by boiling with an alkaline solution of arbitrary strength has been observed in two stages for the purpose of separating its more purely solvent action (continued for five minutes) from what may be termed its degrading action (continued one hour subsequently). These observations throw a certain light on the nature and order of stability of the bodies of which the fibre is composed; and attention will be drawn to this point in regard to the distinctive character of the jute fibre.

(5.) A high percentage of ash-constituents is usually, in plant structures, associated with the presence of gummy or pectic substances; and the relatively small distribution of the latter throughout the wood and bast of plants accords with their low percentage of inorganic constituents. It is to be noted that the *Boehmeria* fibre stands conspicuously high in regard to its ash, and the presence of pectous substances thus indicated is confirmed by the large loss in weight sustained in the boiling alkaline solution.

(6.) Cellulose structures which differ from pure cellulose may be regarded as containing, in addition, (*a*) bodies of the pectic group; (*b*) substances connected with the trihydric phenols; (*c*) substances containing furfural,—the union of these with cellulose being probably such as is known as combination by residues, *i.e.*, to form with the cellulose residue a chemical whole. The groups of compounds under (*a*) (*b*) and (*c*) differ from one another and from cellulose in respect of elementary composition, and its determination is a certain measure of the quantitative relations of these groups to one another. It may be remarked, that (*b*) and (*c*) are in all cases yet observed co-incidental, and agree also in respect of high carbon percentage: consequently as factors in the mean carbon percentage of a fibre they cannot as yet be separated.

(7.) The *chemical* evidence of lignification is the formation of substitution-derivatives on exposure to the action of chlorine gas, and the proof of the formation of these is afforded by their characteristic colour-reaction with solutions of the neutral sulphites.

To sum up these results and bring out more clearly the distinctive character of the jute fibre, I may recapitulate its more striking points of differentiation from the other fibres included in this investigation. (1.) High carbon percentage. (2.) Power of resisting the *continued* action of boiling alkaline solutions, from which, together with the re-

sults of an examination of the substances dissolved, it is to be inferred that the pure fibre contains no constituents of the pectic group. (3.) Such uniformity in composition and properties as to permit us to regard it as a chemical whole. (4.) Its comparative simple microscopic features.

Some of these characteristics are represented amongst the other fibres, but are never united as in the case of jute, which is therefore to be preferred as a simple type of lignification; and over *biologically* complicated structures, such as wood, its superiority is still more manifest.

IV.—*On a Condensation-product of Phenanthraquinone with Ethylic Aceto-acetate.*

By Francis R. Japp, M.A., Ph.D., Assistant Professor of Chemistry in the Normal School of Science, South Kensington, and Fredk. W. Streatfeild.

In a former communication (this Journal, Trans., 1882, 270) we described the acetonquinimide of phenanthrene, $C_{17}H_{15}NO_2$, obtained by the interaction of phenanthraquinone, acetone, and ammonia. In endeavouring to extend this reaction to other ketones, we substituted ethylic aceto-acetate for acetone. No reaction took place at ordinary temperatures, but on heating phenanthraquinone, ethylic aceto-acetate, and concentrated aqueous ammonia for a short time under pressure at 100°, a dark-coloured mass was obtained, from which, by an appropriate process of purification, a compound was isolated, crystallising in needles, and fusing at 184·5—185·5°. (A description of this process of purification is superfluous, as a much better method of preparing the substance is given further on.) The compound did not contain nitrogen. On analysis it yielded figures agreeing with the formula $C_{20}H_{16}O_4$:—

	Substance.	CO_2.	OH_2.
I	0·1488	0·4085	0·0682
II	0·1740	0·4783	0·0790
III	0·1484	0·4079	0·0669

	Calculated for $C_{20}H_{16}O_4$.		Found.			
			I.	II.	III.	Mean.
C_{20}....	240	75·00	74·87	74·96	74·96	74·93
H_{16} ..	16	5·00	5·09	5·04	5·00	5·06
O_4....	64	20·00	—	—	—	(20·01)
	320	100·00				100·00

A compound of this formula would be formed from one molecule of phenanthraquinone and one of ethylic aceto-acetate, by the elimination of one molecule of water.

$C_{14}H_8O_2$	+	$C_6H_{10}O_3$	=	$C_{20}H_{16}O_4$	+	OH_2.
Phenanthra-quinone.		Ethylic aceto-acetate.		New compound.		

The reactions of this compound show that in its formation one atom of oxygen from the quinone is eliminated along with two atoms of hydrogen from the ethylic aceto-acetate, the two resulting dyad groups then uniting by means of the free affinities. From the fact that no such condensation occurs when ethylic diethaceto-acetate is substituted for ethylic aceto-acetate, we may conclude with a high degree of probability that the two hydrogen-atoms thus eliminated are furnished by the methylene group in aceto-acetic acid. The compound would thus possess the formula—

$$\begin{array}{l} C_6H_4\text{—}C\!=\!C\!<\!\begin{array}{l}CO\text{—}CH_3\\COOC_2H_5\end{array}\text{,}\\ \quad|\qquad\quad| \\ C_6H_4\text{—}CO \end{array}$$

and might be termed *ethylic phenanthroxylene-aceto-acetate.**

The reaction is analogous to the condensations of aldehydes with ethylic aceto-acetate described by Claisen (*Ber.*, **14**, 345), in which, however, gaseous hydrochloric acid was employed as a dehydrating agent.

The dehydrating action of aqueous ammonia has not, so far as we are aware, been previously observed. It resembles, however, the dehydrating action of aqueous caustic potash upon acetone described by Heintz (*Annalen*, **196**, 118). Condensations between aldehydes and ketones have also been effected by means of dilute caustic soda (Schmidt, *Ber.*, **14**, 1459; Claisen, *ibid.*, **14**, 2468).

The foregoing analogy led us to examine whether a caustic alkali could not be substituted for ammonia in the above reaction. Not only did this prove to be the case, but the yield by the new method was fully twice as great as when ammonia was employed; whilst, owing to the almost total absence of resinous bye-products, the process of purification was materially shortened.

After several trials the following mode of conducting the experiment was adopted, as yielding the best result:—100 grams of phenanthraquinone, ground to an impalpable powder (this is essential, as larger particles escape conversion), are introdnced into a flask with

* The dyad radical $(C_{14}H_8)''$ is *phenanthrylene;* the dyad radical $(C_{14}H_8O)''$ may be styled *phenanthroxylene.*

90 grams (an excess) of ethylic aceto-acetate; 150 c.c. of dilute potash (1 part of solid caustic potash to 6 of water) are now added, and the mixture is gently warmed, agitating all the time. The reaction takes place quickly with considerable rise of temperature, and the orange colour of the quinone disappears, giving place to the light grey of the crude condensation-product. The product is boiled with water, washed with alcohol, and crystallised from boiling benzene till the fusing point remains constant.

From 100 grams of quinone over 100 grams of a product, once crystallised from benzene and practically pure, were obtained.

Gaseous hydrochloric acid does not effect the condensation of phenanthraquinone with ethylic aceto-acetate.

Properties.—Ethylic phenanthroxylene-aceto-acetate is deposited from its hot benzene solution in tufts of fine white silky needles. It fuses with blackening and evolution of gas at 184·5—185·5°. It is soluble also in alcohol and in glacial acetic acid. On oxidation with a chromic mixture it yields phenanthraquinone.

Hot caustic potash decomposes it, yielding a purple or a green solution, according to the concentration of the potash. Dilute potash appears to saponify it slowly in the cold. These reactions have yet to be studied.

With bromine in acetic acid solution it appears to form, after long standing, an addition-product. This product, which is much less soluble in acetic acid than the original compound, is slowly deposited from the solution. By recrystallisation from hot glacial acetic acid it was obtained in flat yellow needles. The fusing point could not be determined, as the substance, without previously fusing, became quite black at about 150°. A bromine determination gave figures agreeing with the formula $C_{20}H_{16}O_4Br_2$ (Br calculated, 33·33; found, 33·84 per cent.). Of course analysis is incompetent to decide between this formula and the formula of a substitution compound $C_{20}H_{14}O_4Br_2$; but judging from the analogy of the compounds discovered by Claisen, the probability is greatly in favour of the first formula. The usual method of deciding this question by determining the quantity of bromine requisite for the formation of the compound is scarcely applicable in the present case, owing to the extreme slowness with which the compound is formed. In the case of the condensation-product of chloral with ethylic aceto-acetate, Matthews (*Dissertation*, Bonn, 1882, p. 28) observed a similar sluggishness in the way in which this compound combined with bromine.

Action of Hydriodic Acid upon Ethylic Phenanthroxylene-aceto-acetate.—A quantity of the above compound was mixed with amorphous phosphorus in a flask, and an excess of fuming hydriodic acid was added. A reaction took place, accompanied by a rise of temperature, and the

substance fused to a black pitchy mass. This product, which became semi-solid on cooling, was washed successively with water, with cold alcohol, and with small quantities of ether. The brownish substance which now remained was dissolved in boiling alcohol, and the solution filtered from unchanged amorphous phosphorus. The alcoholic solution deposited on cooling a granular substance, which by repeated crystallisation was obtained in star-shaped aggregations of a pink colour. This colour is due to an impurity, and is best got rid of by dissolving the crystals in boiling light petroleum. On allowing the petroleum solution partially to cool, the colouring matter separates out first on the sides of the vessel, and the solution, when poured off at the proper moment, deposits almost colourless crystals. A final crystallisation from benzene removes the last traces of colour. The pure substance fused at 124°.

We found that the pink-coloured substance could be bleached by exposing it in solution to the action of daylight.

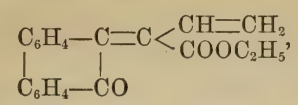
The above somewhat complicated process of purification so diminished the quantity of substance, that from 60 grams of ethylic phenanthroxylene-aceto-acetate only 4 grams of the pure reduction-product were obtained.

The compound contained no iodine. Analysis of different preparations yielded numbers corresponding with the formula $C_{20}H_{16}O_3$:—

	Substance.	CO_2.	OH_2.
I	0·1334	0·3849	0·0658
II	0·2020	0·5836	0·0955
III	0·1429	0·4126	0·0701

	Calculated for $C_{20}H_{16}O_3$.		Found.			
			I.	II.	III.	Mean.
C_{20}....	240	78·95	78·68	78·79	78·75	78·74
H_{16} ..	16	5·26	5·48	5·25	5·45	5·39
O_3....	48	15·79	—	—	—	(15·87)
	304	100·00				100·00

The hydriodic acid had therefore removed one atom of oxygen from the compound $C_{20}H_{18}O_4$. This process may be most readily explained by supposing that the acetyl-group of the ketonic acid is first reduced to the group $CH_3—CH(OH)—$, which then parts with water, and is converted into the vinyl-group $CH_2{=}CH—$. This hypothetical intermediate compound would be a derivative of β-hydroxybutyric acid, and the ease with which this acid parts with the elements of water, and is converted into crotonic acid is well known. According to this view the reduction-compound would possess the constitution—



and to this compound the name *ethylic α-phenanthroxylene-isocrotonate* might be given.

That it is not the oxygen-atom of the phenanthroxylene-group which is removed during the reduction, is very clearly shown by the behaviour of the reduction-product towards caustic alkalis (*vide infra*).

The same reduction-compound is obtained when the condensation-product is treated in acetic acid solution with zinc-dust; but the yield by this method does not appear to be so good as when hydriodic acid is employed.

The reduction-compound forms with bromine in acetic acid solution a compound—probably additive—which has not been examined.

On oxidation with a chromic mixture the reduction-compound yields phenanthraquinone.

On heating between watch-glasses it yields a sublimate of a new compound, in the form of white needles, fusing at 213°, the examination of which is described later. A portion of the substance remains as a charred mass.

By heating ethylic phenanthroxylene-aceto-acetate with fuming hydriodic acid and amorphous phosphorus to 200°, a second reduction-compound was obtained, in the shape of an acid. Mineral acids precipitated it from the solutions of its salts as an amorphous substance, insoluble in all the ordinary organic solvents. Neither the acid nor its salts could be obtained in a crystallised condition, so the further investigation of this substance was abandoned.

Behaviour of Ethylic Phenanthroxylene-isocrotonate towards Caustic Alkalis.—Solutions of alkaline carbonates are without action upon this compound, but dilute caustic potash dissolves it readily on gently warming. On adding hydrochloric acid to an alkaline solution thus prepared, a new organic acid was precipitated. This acid was almost insoluble in alcohol and other organic solvents of low boiling point, but boiling phenol dissolved it readily, and on carefully diluting the hot solution with alcohol, the acid separated in fine colourless needles, which, after washing with alcohol and drying, fused at 295°. This fusing point was not altered by a second crystallisation from phenol.

The results of analysis agreed with the formula $C_{18}H_{14}O_4$:—

	Substance.	CO_2.	OH_2.
I.....	0·1144	0·3078	0·0486
II.....	0·1282	0·3446	0·0542

	Calculated for $C_{18}H_{14}O_4$.		Found.		
			I.	II.	Mean.
C_{18}.....	216	73·47	73·37	73·27	73·32
H_{14}	14	4·76	4·72	4·70	4·71
O_4.....	64	21·77	—	—	21·97
	294	100·00			100·00

The caustic alkali had therefore not merely saponified the ethylic phenanthroxylene isocrotonate, but had at the same time effected the addition of the elements of a molecule of water to the acid thus produced:—

$C_{20}H_{16}O_3 + OH_2 = C_{18}H_{12}O_3 + C_2H_6O$.... (Saponification),

and

$C_{18}H_{12}O_3 + OH_2 = C_{18}H_{14}O_4$..... (Addition of water).

New acid.

An examination of the salts of this acid disclosed the remarkable fact that the acid was dibasic, assuming, as is unavoidable from the mode of formation of the compound and from its reactions, that the molecular formula is that given above, and not half this formula.

Silver Salt.—This was obtained as a white crystalline insoluble precipitate by adding silver nitrate to a neutral solution of the ammonium salt. It yielded the following numbers on combustion:—

Substance.	CO_2.	OH_2.	Ag.
0·1727	0·2687	0·0381	0·0733

	Calculated for $C_{18}H_{12}O_4Ag_2$.		Found.
C_{18}.....	216	42·52	42·43
H_{12}.....	12	2·37	2·45
Ag_2	216	42·52	42·44
O_4	64	12·59	(12·68)
	508	100·00	100·00

Barium Salt.—This salt was prepared by precipitating the ammonium salt with barium chloride. It formed a white, insoluble, crystalline powder. Determinations of barium and water of crystallisation gave numbers agreeing with the formula $C_{18}H_{12}O_4Ba,2OH_2$—Ba (in crystallised salt): Found, 29·39; calculated, 29·46 per cent. OH_2 (not entirely expelled below 220°, at which temperature the salt becomes slightly dark-coloured): Found, 8·33; calculated, 7·74 per cent. A slight decomposition had therefore probably taken place. At 180° only 1 mol. of water of crystallisation is expelled.

The acid may therefore be formulated $C_{16}H_{12}(COOH)_2$. It does not,

like the two compounds already described, yield phenanthraquinone on oxidation. We repeated the oxidation under varying conditions, but on no occasion was a trace of the easily recognisable quinone formed. This negative result is of importance, as it renders it probable that in the formation of the dibasic acid the closed lateral chain of the phenanthrene-group is severed. An inspection of the formula of ethylic phenanthroxylene-isocrotonate shows that it is in fact not possible to obtain from this substance by saponification and simultaneous addition of the elements of water a dibasic acid without thus severing the closed chain. The quantity of substance at our disposal was insufficient to allow of our studying the oxidation-products of the acid.

Heated between watch-glasses, the acid yielded a sublimate of colourless needles fusing at 213°, identical with the sublimate obtained from ethylic phenanthroxylene-isocrotonate. A portion of the substance was charred in the process; but the yield of sublimate was better than in the former case. A quantity of this sublimate was therefore prepared from the acid. It was purified by crystallisation from boiling alcohol, in which it dissolves readily, separating out almost entirely on cooling. It was thus obtained in fine colourless silky needles, fusing, as above, at 213°. Analysis gave results agreeing with the formula $C_{14}H_{10}O$:—

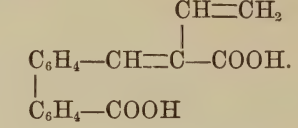
Substance.	CO_2.	OH_2.
0·0672	0·2134	0·0326

	Calculated for $C_{14}H_{10}O$.		Found.
C_{14}	168	86·60	86·60
H_{10}	10	5·15	5·39
O	16	8·25	(8·01)
	194	100·00	100·00

We were not able to examine this substance further, except to ascertain that it is insoluble both in caustic alkalis and in hydrogen sodium sulphite. The small quantity at our disposal sufficed only for a single analysis, and the preparation of the substance in any quantity would be a work of very great labour. To judge from the ease with which the substance sublimes, the above simple formula is probably also its molecular formula.

Constitution of the Dibasic Acid.—There are two ways in which a compound of the formula of ethylic phenanthroxylene-isocrotonate may by the action of caustic alkali be converted into a dibasic acid. The simplest explanation of the phenomenon consists in supposing that, along with the saponification of the $COOC_2H_5$ group, the carbonyl-group of phenanthroxylene is separated from the other carbon-atom of the closed lateral chain; potassoxyl then attaches

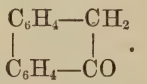
itself to the vacant affinity of the carbonyl, converting it into COOK, whilst the remaining hydrogen-atom from the potassium hydroxide satisfies the vacant affinity of the other carbon-atom of the severed lateral chain. The acid would thus possess the constitution represented by the formula—



The second mode of regarding the reaction is to suppose that an intramolecular migration takes place similar to that in which phenanthraquinone is converted by the action of caustic potash into diphenyleneglycolic acid, a reaction in which the phenanthraquinone takes up the elements of a molecule of water, whilst one of its carbonyl-groups is converted into carboxyl. On this assumption the dibasic acid would be a derivative of diphenylene-methane.

We think, however, that this last view is to be rejected. The fact that both ethylic phenanthroxylene-isocrotonate and the dibasic acid yield under the influence of heat the same compound, $C_{14}H_{10}O$, points to an analogous constitution of the two compounds, a condition which is not fulfilled by representing the one as a derivative of phenanthrene and the other as a derivative of diphenylenemethane. Rejecting therefore this view, there remains for our acceptance the formula above given.

A possible constitution for a compound $C_{14}H_{10}O$, derived both from ethylic phenanthroxylene-isocrotonate and from the dibasic acid, would be—



Such a compound would stand in the same relation to phenanthraquinone in which deoxybenzoïn stands to benzil. An investigation of the reactions of this compound would doubtless have been desirable, and would possibly have thrown light upon the constitution of the compounds from which it is derived. We have already alluded to the difficulties which would attend such an investigation.

The chief value of the facts here described lies in their bearing upon the constitution of phenanthraquinone. The formation of such a compound as ethylic phenanthroxylene-aceto-acetate from ethylic aceto-acetate and phenanthraquinone, furnishes a very strong argument in favour of Fittig's formula for phenanthraquinone as against that of Graebe.

The investigation will be continued.

V.—*Note on the Preparation of Diphenylene Ketone Oxide.*

By W. H. Perkin, Ph.D., F.R.S.

Whilst making experiments with the hope of preparing the anhydride of salicylic acid, $\begin{matrix} C_6H_4 \\ | \\ CO- \end{matrix}\!\!>\!O$, a quantity of salicylic acid was heated with acetic anhydride. On boiling the mixture, the acid dissolved, acetic acid and the excess of acetic anhydride used distilling off. A viscid liquid then remained in the retort, solidifying on cooling to a glass-like mass, undoubtedly consisting chiefly of salicylide. On submitting this to distillation, a considerable quantity of an oily product came over, solidifying in the neck of the retort to a crystalline mass. This on being washed with alcohol, and purified two or three times by crystallisation from that solvent, was obtained in the form of fine pale-yellow needles. On analysis this substance gave the following numbers:—

I. 0·1450 gram of substance gave 0·4222 of CO_2 and 0·0571 of OH_2.
II. 0·1488 „ „ 0·4335 „ 0·0559 „

These give percentages agreeing with the formula $C_{13}H_8O_2$.

	Theory.	Experiments. I.	Experiments. II.
Carbon	79·59	79·41	79·45
Hydrogen ..	4·08	4·37	4·17

It fuses at 173·5° C.

This substance is evidently the same as that obtained by Merz and Weith (*Ber.*, **14**, 187) by the oxidation of methylene-diphenyl oxide, also by R. Richter (*J. pr. Chem.*, N.F., **23**, 349) by distilling basic potassium salicylate with phosphorus oxychloride. This latter process, however, yields it, so far as I have experimented with it, in only comparatively small quantities, whereas by the method above described, from 30 to 40 per cent. of the theoretical quantity is obtained. Its formation from salicylide may be represented thus:—

$$C_6H_4\left\{\begin{matrix} O.CO \\ CO.O \end{matrix}\right\}C_6H_4 = C_6H_4{<}\begin{matrix} CO{-}C_6H_4 \\ | \\ O \end{matrix}\!\!>\!C_6H_4 + CO_2.$$

This substance being now obtainable with comparative ease by the above process, my son, Mr. A. G. Perkin, has commenced the study of its derivatives, and of the secondary bodies which are also obtained in its preparation from salicylic acid.

VI.—*On certain Brominated Carbon Compounds obtained in the Manufacture of Bromine.*

By S. Dyson, Student in the Laboratory of the Yorkshire College, Leeds.

These compounds were contained in a liquor obtained as a bye-product, at the works of the North British Chemical Company.

Mr. Stanford, after making some experiments upon it, forwarded a sample to Dr. Thorpe, who requested me to complete its investigation. Mr. Stanford's experiments led him to believe that the liquid consisted mainly of bromoform.

The presence of this compound was not improbable, since Hermann, many years ago, had shown (*Ann. Chem. Pharm.*, **95**, 211) that a similar liquor, from the bromine obtained from the Schönebeck brine, consisted principally of bromoform, the formation of which he explains by the action of free bromine upon the organic matter contained in the mother-liquor from the brine.

The liquid received from Mr. Stanford was dried by calcium chloride and submitted partly to fractional distillation, and partly to fractional freezing, with the view of isolating these brominated compounds. Le Bel-Henninger tubes were used, in order to effect as complete a separation of the different fractions as possible. The liquid distilled almost entirely between 82° and 172°, some crystals of carbon tetrabromide being observed in the residue left in the flask. The main portion of the distillate consisted of bromoform, a tolerably constant boiling point being obtained at 148—150°.

The fractions next in amount boiled at 121—123° and 123—125°. These were analysed, and proved to consist of chlorobromoform. The analysis was conducted in the usual way by ignition with quicklime, and precipitation of the calcium chloride and bromide from a nitric acid solution with silver nitrate.

0·4015 of the liquid gave 0·7074 AgBr, 0·2916 AgCl, and

0·0079 reduced Ag $=$ { 0·0052 as AgBr $=$ 0·009044 AgBr. / 0·0027 as AgCl $=$ 0·003584 AgCl.

Total AgBr $=$ 0·7164 $=$ 75·97 per cent. Br.

Total AgCl $=$ 0·2952 $=$ 18·20 per cent. Cl.

$CHBr_2Cl$ requires 76·76 per cent. Br and 17·02 per cent. Cl.

Two determinations of vapour-density gave—

I.	II.	
106·2	105·5.	Theory requires 104·2.

The specific gravity at 20° was 2·477. According to Jacobsen and Neumeister (*Ber.*, 1882, 599), the discoverers of chlorobromoform, this body boils at 123—125°, and has a specific gravity at 15° of 2·4450.

The existence of carbon tetrabromide as a bye-product in the manufacture of bromine has already been signalised by Mr. J. C. Hamilton, a former student in this laboratory (*Chem. Soc. J.*, Jan., 1881). The existence of the recently discovered chlorobromoform as a bye-product in this manufacture has, however, been hitherto unnoticed.

VII.—*On Ethylene Chlorobromide and some Compounds obtained from it.*

By J. William James, Ph.D. (Jena), F.C.S., Demonstrator and Lecturer in the Mining School, Bristol.

Preparation of Ethylene Chlorobromide. (Maxwell Simpson's Method.)

Shortly after I had succeeded in obtaining the ethylene chlorothiocyanate from the ethylene chlorobromide prepared by Lössner's method (this Journal, December, 1879), Maxwell Simpson proposed a method for the preparation of the latter compound, which, with some little modification, I have found to work remarkably well and easily, as much as 70 per cent. of pure chlorobromide boiling at 107—109° being obtained. As this method has only been abstracted into the various chemical journals from the *Proceedings of the Royal Society* of London, and since by the discovery that it is possible to replace the bromine only in C_2H_4ClBr by a compound negative radical, a new interest has been given to the mixed haloïd derivatives of the C_nH_{2n} series, I venture to describe it at length:—Dr. Simpson says: "500 grains of bromine (rather over 32 grams) are dissolved (?) in 4 fluid ounces of a mixture of equal volumes of strong hydrochloric acid* and water. The solution is introduced into a flask with a long neck and surrounded with ice. Washed chlorine is then passed into it, with repeated agitation, till it ceases to be absorbed. In this way not a trace of bromine is lost, and no solid hydrates are formed during the passage of the gas. On passing olefiant gas into the solution,

* Both in the original paper and in the Abstracts *hypochlorous acid* is given, which was a printer's error in the first place.

which should be repeatedly agitated and surrounded with cold water, I obtained a large quantity of an oily liquid which I separated from the acid solution, washed with dilute potash, and distilled. Almost the entire quantity passed over between 106° and 110°, most between 108° and 110°."

When first using this method, wishing to obtain a large quantity of chlorobromide, I weighed out 500 grams of bromine and followed the above directions. When the operation was completed a quantity of an oil was obtained which, after washing and drying, boiled at 109—112°, a large portion, however, boiling at 112—115°. The percentage of pure and impure oil obtained was scarcely over 50, while only a few grams distilled at 106—108°, the boiling point of the ethylene chlorobromide obtained by Lössner's method (see this Journal, 1879, Trans., 806).

The portion which distilled at 109—112° was acted upon with potassium thiocyanate, as described in my former paper, when only small quantities of ethylene chlorothiocyanate were obtained, the dithiocyanate, $C_2H_4(SCN)_2$, being chiefly formed. The oil boiling at 112—115° produced no chlorothiocyanate, or at the most mere traces, which, owing to the large quantity of dithiocyanate, I was unable to separate.

In spite of the above facts, I was unwilling to believe that this chlorobromide, although boiling 4° or so higher than that previously used, should have so marked an influence upon the formation of the compound in question; but a number of trials with absolute alcohol satisfied me that such was really the case, since a portion of the chlorobromide obtained by Simpson's method (b. p. 107—108°) formed the chlorothiocyanate in quite as large quantity as by Lössner's. This last experiment convinced me that no isomeric compound was produced, but that probably the chlorobromide of higher boiling point contained an admixture of ethylene dibromide. The numbers obtained by combustion, although not differing very widely from those calculated for pure C_2H_4ClBr, plainly indicated that such was the case, the percentage of carbon and hydrogen being too low.

In order to substantiate this supposition, 200 grams of ethylene dibromide were acted upon with less than the theoretical quantity of antimony pentachloride, viz., 130 grams (calc. 159), when the chlorobromide obtained boiled for the most part at 109—111°, and this produced comparatively small quantities of the chlorothiocyanate.

It occurred to me that the temperature of passing in the chlorine may have an influence upon the final result, both as regards the boiling point and percentage of oil obtained. With a view to confirming this, 200 grams of bromine were placed in a flask, and 24 fluid ounces of hydrochloric acid and water in equal volumes added; the flask was

surrounded with ice in small pieces, and left at rest for half an hour before chlorine was passed in. The temperature inside the flask was just under 2°. On completion of the process 140 grams C_2H_4ClBr, boiling at 107—109°, were obtained.

Other experiments gave even better yields, but on an average not more than 65—70 per cent. of pure substance can be relied on. The percentage of ethylene chlorothiocyanate produced from this compound was quite equal to that given by the chlorobromide of the pentachloride of antimony method, although that substance boils at a slightly lower temperature. It is advisable to let the delivery-tube dip beneath the bromine; if this be so, the chlorine is taken up much more rapidly.

The above results show clearly that the temperature at which the chlorine is passed into the bromine is of paramount importance in obtaining, not only a good yield of chlorobromide, but a compound suitable for further use, although in the latter instance the strength of the alcohol is of equal or perhaps greater importance. This temperature should be as near 0° as possible. The small quantities of bromine used by Simpson left no room for the error which I have pointed out, the mixture being quickly cooled to the required temperature.

Preparation of Ethylene Chlorothiocyanate.

From a large number of experiments, I have found the following method to give the best yield; and although it has in part appeared in this Journal, it is perhaps advisable to recapitulate to some extent.

After digesting the chlorobromide, boiling at 107—109°, with potassium thiocyanate and absolute alcohol, and removing as much of the latter as possible by distillation on the water-bath, the remaining oil was filtered from the separated ethylene dithiocyanate into a small flask, now again distilled until the thermometer showed 120°, left to cool, and then placed in a freezing mixture, by which means nearly the whole of the dithiocyanate crystallised out. It is now only necessary to decant or filter off the oil and distil it in a retort, which should not be filled to more than one-tenth of its capacity, the distillation being conducted *rapidly*. In this way most of the chlorothiocyanate passes over before the decomposition sets in. When the thermometer indicates 170° or thereabouts, the liquid in the retort will have become dark-brown. At this point the receiver should be changed, and all oil coming over between 170° and 210° may be taken as pure enough for the further investigation of its properties. The thermometer rises rapidly to 200°, and nearly the whole of the liquid distils between 200° and 205°. The receiver should be removed before 210°, as at that temperature a sudden decomposition

takes place with much frothing, pungent vapours being evolved which cause violent sneezing and lacrimation.

The distressing effect exerted by the products of the above decomposition upon the nose and eyes made it desirable to prevent, as far as possible, the occurrence of this decomposition. The distillation was accordingly conducted slowly by constantly removing the Bunsen; this, however, only made matters worse, as the decomposition set in before scarcely half the oil had passed over; neither did distilling in a vacuum obviate it.

Ethylene chlorothiocyanate dissolves in hot water from which it separates unaltered on cooling. Concentrated sulphuric acid dissolves it, and on warming it becomes decomposed with evolution of sulphurous anhydride. It is soluble also in hydrochloric acid, but suffers no alteration on warming.

On digesting it with an alcoholic solution of potassium thiocyanate, ethylene dithiocyanate, $C_2H_4(SCN)_2$, is produced.

This compound has a burning taste, and blisters the skin; sp. gr. 1·28 at 15° C. For other properties, see this Journal, December, 1879.

Action of Sodium Sulphite upon Ethylene Chlorothiocyanate.

Formation of Ethylene-thiocyanosulphonic Acid, $C_2H_4{<}\begin{matrix}SO_3H\\SCN\end{matrix}$.

The sodium salt of this new acid may be obtained, mixed with more or less sodium chloride and sulphate, by digesting the chlorothiocyanate of ethylene with normal sodium sulphite upon the sand-bath; but a far more advantageous method is the following, although I have failed to separate the salt from the above-named impurities:— 20 grams of $C_2H_4Cl(SCN)$ were placed in a stoppered cylinder with 20 grams of crystallised normal sodium sulphite, the aqueous solution of the latter being not too concentrated. In a few moments the liquid turned pink, changing to carmine in less than an hour. The cylinder was now exposed to the direct rays of the sun, and frequently shaken. In the course of a day or so all the oil was taken up, a brown amorphous substance having formed. The liquid, which had become dark brown, was shaken up with animal charcoal, and the filtrate, which was now almost colourless, was evaporated to dryness, with addition of a little dilute hydrochloric acid. The residue was dissolved in water, and a portion of the sodium chloride and sulphate removed by crystallisation. One of the many samples I have made was analysed, and the results obtained tend to show that the sodium salt of a new acid was present in the solid to the extent of about 60 per cent.

The following equation expresses its formation :—

$$Cl.C_2H_4.SCN + Na_2SO_3 = NaSO_3.C_2H_4.SCN + NaCl.$$

The mixture of salts contained 24·35 per cent. NaCl, and 16·00 Na_2SO_4. The sum of these impurities being subtracted, two nitrogen estimations gave 7·84 and 7·48 per cent., while the formula—

$$SO_3Na.C_2H_4.SCN,$$

requires 7·40 per cent.

The mixture of salts was exceedingly deliquescent. Concentrated nitric acid had a violent action upon it; an acid salt of ethylene-disulphonic acid being probably produced, $SO_3Na.C_2H_4.SO_3H$.

The facility with which chlorethylsulphonic acid may be produced from ethylene chlorothiocyanate by oxidation with fuming nitric acid, has led me to prepare a few of its salts and the chloride.

Salts of β-Chlorethylsulphonic Acid.

The name β-chlorethylsulphonic acid is chosen in order to bring out the analogy between this acid and β-chlorpropionic acid, as shown by the following formulæ :—

CH_2Cl	CH_2Cl
|	|
$CH_2CO(OH)$	$CH_2SO_2(OH)$
β-Chlorpropionic acid.	β-Chlorethylsulphonic acid.

Potassium salt, $C_2H_4ClSO_3K$.—A solution of potassium sulphate was added to one of chlorethylsulphonate of barium until no further precipitate formed. The filtrate, after concentration, yielded fine needles, which contained no water of crystallisation. It is insoluble in absolute alcohol and ether.

Strontium salt $(C_2H_4ClSO_3)_2Sr + 2OH_2$, may readily be prepared by acting upon an aqueous solution of the acid with excess of strontium carbonate suspended in water. The filtrate, on evaporation, yielded acicular crystals which contained 2 mols. of water.

An analysis gave the following numbers :—

I. 0·1896 gram of the crystallised salt, dried between blotting-paper, lost 0·017 gram at 100°.

II. 0·2842 gram, after heating to redness and treating with sulphuric acid, gave 0·1252 gram $SrSO_4 = 0·05969$ Sr.

	Calculated.	Found.
Sr	21·29 per cent.	21·00 per cent.
$2H_2O$	8·76 „	8·96 „

Zinc salt $(C_2H_4ClSO_3)_2Zn + 6OH_2$.—This salt was obtained by

adding an aqueous solution of the sulphate to the barium salt of the acid. It crystallises in laminæ, and is insoluble in absolute alcohol and ether, but dissolves in weak alcohol. That it crystallises with 6 mols. of water, is proved by the following analysis:—

0·094 gram of air-dried salt, lost by heating to 100° 0·022 gram of water = 23·40 per cent. H_2O: calculated for $6H_2O$ 23·47 per cent.

Copper salt $(C_2H_4ClSO_3)_2Cu + 4OH_2$.—This salt, prepared by adding a solution of copper sulphate to the barium salt, may be obtained in fine square blue tablets of the triclinic system, by slow evaporation of its solution. After powdering and pressing between filter-paper, the salt was analysed, and the results show that it crystallises with 4 mols. of water, two of which it loses at 100°, becoming lighter in colour; the remainder at 120—125°, when it is white. Heated above 125° it undergoes slight decomposition.

I. 0·338 gram salt lost 0·032 gram at 100°, and on heating to 125°, the total loss was 0·0575 gram.

II. 0·3015 gram lost 0·0280 gram at 100°, and at 125° 0·048 gram.

Calculated.	Found. At 100°.	At 125°.
$(C_2H_4ClSO_3)_2Cu + 4H_2O$. $2H_2O$ 8·53 p. c.; $4H_2O$ 17·06 p. c.	(I) 9·46	16·86
	(II) 9·28	16·08

This salt may be obtained crystallised in laminæ of a light blue colour from concentrated solutions. It is insoluble in alcohol and ether, but dissolves without difficulty in water, which solution may be boiled without decomposing.

β-Chlorethylsulphonic chloride, $C_2H_4ClSO_2Cl$.—This substance was obtained from the potassium salt by the action of phosphorus pentachloride. It boils 200—205°.

Action of dry Ammonia upon an ethereal solution of the Chloride.—An oily liquid is formed, containing nitrogen and sulphur, but no chlorine; the composition of which has not yet been determined.

As the above reaction did not appear to yield any amide, it seemed interesting to study the preparation of the amide of another sulphonic acid, since, so far as I have been able to ascertain, no amides of these acids have been obtained, with the exception of the aromatic compounds.

Preparation of the Amide of Ethylsulphonic Acid, $C_2H_5SO_2NH_2$.—The acid obtained by oxidation of ethyl thiocyanate with red fuming nitric acid, was neutralised with potassium carbonate, and its potas- salt treated with phosphorus pentachloride. 60 grams of the ethyl-

sulphonic chloride thus obtained were dissolved in anhydrous ether, and ammonia was passed in to saturation. On the ethereal solution evaporating, long, glittering, prismatic crystals, began to separate. These were removed and dried in a vacuum.

An estimation of the carbon and hydrogen gave this result:—

Calculated for $C_2H_5SO_2NH_2$.		Found.
C	22·01 per cent.	22·70 per cent.
H	6·42 „	7·46 „

These numbers not agreeing with the calculated as well as could be wished, the substance was recrystallised from ether, and a nitrogen determination showed that it was now in a state of purity.

0·4080 gram on combustion with CuO, $PbCrO_4$, and Cu, gave 48 c.c. of nitrogen at a temperature of 26° C., and 754 mm. pressure.

Calculated.		Found.
N	12·84 per cent.	12·86 per cent.

Absolute alcohol was substituted for the ether in the preparation of this amide, but the ammonium salt of ethylsulphonic acid was produced.

The amide of ethylsulphonic acid is soluble in water, alcohol, and ether. From its solution in either of these solvents it may easily be obtained in the crystalline form, which is usually that of fine silky needles. By slow evaporation, however, of its ethereal solution, it may be obtained in well-defined prisms. It does not combine with hydrochloric acid or platinic chloride. It melts at 58° (uncorr.) to a clear colourless liquid, and when heated on platinium foil suffers decomposition.

Action of Normal Sodium Sulphite on Ethylene Dibromide.

Some years ago Strecker (*Ann. Chem. Pharm.*, **148**, 90), in his investigation of the action of normal sodium sulphite upon various organic compounds containing chlorine, bromine, and iodine, studied its reaction with ethylene dibromide, and obtained the sodium salt of ethylene disulphonic acid, which was apparently the only organic salt produced in the reaction. My experiments have, however, shown that isethionate of sodium is also produced, although in very small quantity.

When ethylene dibromide or chlorobromide is boiled with an aqueous solution of sodium sulphite, the odour of sulphurous anhydride is distinctly perceptible in a few minutes. On continuing the digestion

until SO_2 ceased to be evolved, the liquid was poured off from the remaining oil, evaporated to dryness, and the residue boiled with strong alcohol. On cooling, laminæ separated, which analysis has shown to consist chiefly of sodium isethionate, mixed with a little sodium bromide. The reaction may be thus formulated :—

$$C_2H_4Br_2 + Na_2SO_3 + OH_2 = OH.C_2H_4.SO_3Na + NaBr + HBr,$$

the evolution of sulphurous anhydride being of course due to the decomposition of a portion of the sodium sulphite by the hydrobromic acid.

One sample gave these numbers on analysis. Bromine was distinctly found in the salt.

		Found.		
Calculated for $C_2H_4OHSO_3Na$.		I.	II.	III.
C.....	16·21	14·19	—	—
H	3·37	2·58	—	—
S.....	21·62	—	19·15	19·02

The following is a summary of the principal results described in the foregoing pages :—

1. In preparing ethylene chlorobromide by passing the gas into a solution of chloride of bromine (ClBr), it is necessary, in order to obtain a pure product and good percentage, that the chlorine be passed into the bromine at a temperature of about 0° ; otherwise a substance is formed boiling some 3° or 4° higher than pure C_2H_4ClBr, which is useless for the advantageous preparation of ethylene chlorothiocyanate.

2. If an aqueous solution of neutral sodium sulphite and ethylene chlorothiocyanate be brought together in direct sunlight, the sodium salt of a new acid, viz., ethylene-thiocyanosulphonic acid, $C_2H_4<\begin{matrix}SO_3H\\SCN\end{matrix}$, appears to be produced.

3. By passing ammonia gas into an ethereal solution of chlorethyl-sulphonic chloride, no amide is formed ; with ethyl-sulphonic chloride, however, the corresponding amide is easily obtained.

4. By the action of neutral sodium sulphite in aqueous solution upon ethylene dibromide or chlorobromide, isethionate of sodium is apparently produced, with evolution of sulphurous anhydride, in addition to the well-known ethylene-disulphonate of sodium obtained by Strecker.

VIII.—*On the Condensation-products of Œnanthaldehyde* (Part I).

By W. H. Perkin, Junr., Ph.D.

Among the many researches on the condensation of the aldehydes, it may be well to mention a few on account of their special bearing on this investigation.

Urech (*Ber.*, **13**, 483, 590, and **12**, 190) found that by the action of dry potassium carbonate on isobutaldehyde, a polymeride of that body is formed, to which he gives the formula $(C_4H_8O)_3$. On distillation, it decomposes into isobutaldehyde, $C_{12}H_{22}O_2$, and other condensation-products, at the same time losing water.

Demtschenko (*Ber.*, **6**, 1176) obtained from isobutaldehyde by the action of sulphuric acid a polymeride which has also the formula $(C_4H_8O)_3$, and which he names *paraisobutaldehyde*. This body is, however, not decomposed on distillation.

Borodin (*Ber.*, **6**, 982) found that by the action of caustic alkali on isovaleraldehyde at 0°, a polymerised modification of that body is formed, which decomposes on distillation, with separation of water, into $C_{10}H_{18}O$, and another condensation-product, $C_{20}H_{38}O_3$, both of which are oils. This last body is decomposed by heating with alkalis into isovaleric acid, isopentylalcohol, and isovaleraldehyde, which bodies are also formed by heating isovaleraldehyde alone to 240°, or with zinc-turnings to 180°.

If isovaleraldehyde is allowed to stand for some time with soda, a hydrate of the formula $C_{20}H_{42}O_5 = (C_{10}H_{20}O_2)_2H_2O$ is formed, which on distillation is decomposed into isovaleraldehyde and the condensation-products $C_{10}H_{18}O$ and $C_{20}H_{38}O_3$. By the action of sodium on isovaleraldehyde, Borodin (*Jahresb.*, 1864, 338; *Ber.*, **5**, 481) obtained the condensation-products $C_{10}H_{18}O$ and $C_{20}H_{38}O_3$, polyisovaleraldehyde, and the alcohol $C_{10}H_{22}O$.

This last body gives on oxidation isocapraldehyde, the acid $C_{10}H_{18}O_2$, an oil which boils at 250—290°, and to which Borodin ascribes the formula $(C_{10}H_{18}O)_n$, also isovaleric acid and isopentylalcohol.

Grenier (*Jahresb.*, 1866, 465) obtained the same body, $C_{10}H_{18}O$, by the action of sodium on ethylisovalerate.

Gass and Hell found that dry potassium carbonate has, at the ordinary temperature, the same action on isovaleraldehyde as caustic potash, but that if the aldehyde is boiled with potassium carbonate, the bodies $C_{10}H_{18}O$, $C_{15}H_{28}O_2$, and $C_{20}H_{38}O_3$, are formed. This last

body on distillation decomposes with separation of water, and gives the aldehyde $C_{10}H_{18}O$.

Of the researches on the condensation-products of oenanthaldehyde, those of Borodin, Bruylants, Tilley, Fittig, and Schiff may be cited.

Borodin found (*Ber.*, **5**, 481) that by the action of caustic alkalis on œnanthaldehyde at ordinary temperatures, two polymeric modifications are formed. One is a solid and the other an oil. They both give off water on distillation, with formation of $C_{14}H_{26}O$ and $C_{28}H_{54}O_3$.

By heating œnanthaldehyde at 240°, the same bodies are formed.

Bruylants (*Ber.*, **8**, 415) obtained by the action of potassium carbonate on œnanthaldehyde, a polymeric modification, which he purified by washing with water and repeatedly crystallising. It melts at 51—52°. Like the polymerides of isobutyl and isovaleryl aldehydes, it decomposes with separation of water on distillation, condensation-products being formed; one of these boils at 160—170°, and appears to be an aldehyde.

Fittig (*Annalen*, **117**, 76) found that if œnanthaldehyde is left in contact with quicklime, heptoic acid, heptyl alcohol, and the hydrocarbons C_7H_{14}, C_8H_{16}, C_9H_{18}, and œnanthacetone, $C_{13}H_{26}O$, are formed.

Tilley (*Jahresb.*, **1**, 566) obtained, by warming œnanthaldehyde with caustic potash to 120°, an oil, $C_{14}H_{28}O$, which boiled at 220°. By the action both of fused caustic potash and also of aqueous potash on œnanthaldehyde, he found that heptoic acid is formed. In the latter case, an oil was separated from the potassium salt by distilling in steam, and was then found to have the boiling point 220°, and on analysis numbers were obtained which seemed to show it to be the same body, $C_{14}H_{28}O$, mentioned above. By oxidation with nitric acid it gives heptoic acid, and by the action of potash heptoic acid is also produced, and a tarry body, hydrogen being evolved at the same time.

Schiff found that by saturating an alcoholic solution of œnanthaldehyde with hydrochloric acid gas, a body of the formula

$$Cl(C_7H_{14})OC_2H_5$$

is formed, which on distillation is completely decomposed into $C_{14}H_{26}O$ and other bodies.

Rieth and Beilstein (*Jahresb.*, **16**, 478) obtained the same body, $C_{14}H_{26}O$, by the action of zinc-ethyl on œnanthaldehyde.

As in many cases in the above-mentioned researches the formulæ only, and not the properties of the bodies obtained, are described, I undertook, at the suggestion of Professor Wislicenus, the following research, in order, if possible, to obtain some clue to the constitution of the bodies formed by the condensation of the aldehydes, and more especially of those derived from œnanthaldehyde.

The œnanthaldehyde used in the following experiments was obtained

from Kahlbaum, in Berlin. It boiled between 150° and 160°. Pure œnanthaldehyde was found to boil at 153—154° (thermometer in vapour), and has the specific gravity

at 15° = 0·8231
at 30 = 0·8128
at 35 = 0·8099

compared with water at the same temperatures.

Action of Potash on Œnanthaldehyde.

The action of potash on this aldehyde is extremely violent. If œnanthaldehyde is mixed with a concentrated solution of potash in alcohol, the rise of temperature, chiefly owing to condensation, is so great as often to cause the alcohol to boil. The products of this reaction consist mainly of potassium heptoate and high condensation-products which, owing to their high boiling points, could not be isolated and examined. However, after many experiments, it was found that if a very dilute solution of alcoholic potash is used, the reaction is less complicated, the following method of procedure giving the best results:—

3 grams of potash were dissolved in about 200 grams of absolute alcohol, and then 200 grams of œnanthaldehyde slowly added, care being taken that the temperature did not rise above 30°, otherwise the reaction was found to go too far, large quantities of high-boiling bodies being produced. The condensation of the œnanthaldehyde takes place very rapidly, and is probably finished in half an hour. At the end of about 24 hours not a trace remains unchanged.

In order to isolate the products of the reaction, the alcohol was first distilled off and then water added, or the product was directly diluted with much water. In either case it was found necessary to shake up the product with ether to perfectly separate the oil from the alkaline solution. The ethereal solution was well washed, first with dilute hydrochloric acid, and then with water, and finally dried over calcium chloride.

The following is the examination of the aqueous alkaline solutions from a number of these operations. They were first treated two or three times with ether to remove traces of oil, saturated with carbonic anhydride to convert any caustic alkali present into carbonate, and evaporated to dryness on a water-bath. The product was then further dried and several times extracted with absolute alcohol.

After the alcohol had been distilled off from these extracts, the saline residue was dissolved in water, acidified with hydrochloric acid, and the acids thus liberated separated with ether, the ethereal solu-

tion was then fractioned. After the ether had been distilled off, the greater part of the product came over between 180° and 230°. A small quantity, however, referred to further on, was left in the retort.

The portion boiling between 180—230°, on fractioning, came over mostly between 220—225°, and was, doubtless, heptoic acid. It gave on analysis the following numbers :—

0·2389 substance gave 0·2372 OH_2 and 0·5659 CO_2.

	Found.	Theory, $C_6H_{13}COOH$.
C	64·60 per cent.	64·61 per cent.
H	11·03 „	10·77 „

The small residue left in the retort was distilled *in vacuo*, and then fractioned under a pressure of 200 mm., when it came over without the least decomposition. The best fraction which could be obtained boiled, at this pressure, between 270—290°, and gave the following numbers on analysis. These agree fairly well with the calculated percentages for an acid of the formula $C_{14}H_{26}O_2$:—

0·1405 substance gave 0·1445 OH_2 and 0·3811 CO_2.

	Found.	Theory, $C_{14}H_{26}O_2 = C_{13}H_{25}COOH$.
C	73·97 per cent.	74·33 per cent.
H	11·42 „	11·50 „

The yield of this acid is perhaps improved by adding hydrochloric acid and extracting the acids directly from the crude potash-salt, instead of saturating with carbonic anhydride, extracting with alcohol, &c., as long boiling seems to decompose the potassium salt. The properties and salts of this acid are described further on, under the heading "Action of Potash on the Aldehyde $C_{14}H_{26}O$."

The following is the examination of the ethereal solution of the oily condensation-products. After the ether had been distilled off the remaining oil was carefully fractioned in a stream of carbonic anhydride.* The thermometer rose rapidly to 260°, between which temperature and 300° by far the largest quantity of the product distilled over as an almost colourless oil, leaving a black residue in the retort which is referred to further on. This distillate was then repeatedly fractioned, the greatest care being taken to prevent the product from coming in contact with the air. An oil at last was obtained boiling between 277° and 279°.

On analysis it gave the following numbers :—

* It is very important to bear in mind that, owing to the rapid absorption of oxygen from the air by these products, all operations with them must be conducted in an atmosphere of carbonic anhydride.

I .. 0·1796 gram substance gave 0·1979 OH_2 and 0·5301 CO_2.
II .. 0·1599 „ „ 0·1812 „ 0·4676 „
III .. 0·1890 „ „ 0·2146 „ 0·5539 „

	Found.				
	I.	II.	II.		Theory, $C_{14}H_{26}O$.
C	80·49	79·74	79·92	per cent.	80·00 per cent.
H	12·24	12·59	12·61	„	12·38 „

These combustions were made from three different preparations. This body has therefore the composition $C_{14}H_{26}O$, and is apparently the same substance as that obtained by Borodin, Schiff and Rieth, and Beilstein. It is a colourless oil, having a faint smell and a burning taste. It does not solidify at $-20°$. Its specific gravity is—

at 15° = 0·8494
at 30 = 0·8416
at 35 = 0·8392

compared with water at the same temperatures.

It absorbs oxygen very rapidly, so much so, that when placed in a tube full of air, over mercury, in a short time nothing but nitrogen is left in it. This oil reduces a solution of Ag_2O in ammonia very easily.

It is an aldehyde, and combines, though very slowly, with hydrogen sodium sulphite, so that, only after keeping the two in contact for months, with frequent agitation, a definite body was obtained; it then had the form of silky crystals slightly soluble in water; it is apparently decomposed by a solution of sodium carbonate. This compound was filtered from the excess of hydrogen sodium sulphite, pressed between filter-paper, and in order to insure its freedom from inorganic matter, two or three times wetted with water and again pressed.

It was then thoroughly dried, and washed with ether to remove any uncombined oil. When pure it is a beautiful silky-looking crystalline substance. A sodium determination gave the following numbers:—

0·4622 gram substance gave 0·1105 gram Na_2SO_4 = 7·74 per cent. Na.

The formula $C_{14}H_{26}O,NaHSO_3$ requires 7·32 per cent.

This aldehyde is soluble in ether, alcohol, carbon disulphide, and glacial acetic acid, in 50 per cent. acetic acid it is only sparingly soluble. It is evidently formed by the elimination of the elements of water from 2 mols. of œnanthaldehyde, according to the equation—

$$2C_6H_{13}COH = C_{13}H_{25}COH + OH_2.$$

The condensation-products boiling above 300°, which were left in the retort after distilling off the aldehyde, $C_{14}H_{26}O$, just described, were very thick ; they were first distilled in a vacuum, and then fractioned under a pressure of 350 mm. The principal portion came over between 320—350°, above that temperature, however, there remained a considerable quantity in the retort, which could not be purified. The product boiling between 320—350° was very carefully fractioned under the same pressure, till at last the principal quantity was obtained, boiling between 330—340°. It is a thick light yellow oil, and has a disagreeable smell and burning taste. It does not solidify at −20°. It mixes in all proportions with the usual solvents, and reduces ammoniacal silver solution.

The analyses gave the following numbers :—

I ..	0·2298	gram	substance	gave	0·2645	OH_2 and	0·7064 CO.
II ..	0·1864	„	„		0·2130	„	0·5723 „
III ..	0·2076	„	„		0·2377	„	0·6433 „
IV ..	0·2347	„	„		0·2663	„	0·7229 „

	Found.				Calculated for $C_{28}H_{50}O$.
	I.	II.	III.	IV.	
C ..	83·83	83·73	83·72	84·00 per cent.	83·58 per cent.
H ..	12·78	12·69	12·60	12·60 „	12·43 „

Nos. I and IV were from the first experiment, Nos. II and III from one made later on. The above results show that the body has the formula $C_{28}H_{56}O$. Its specific gravity is—

at 15° = 0·8831
at 30 = 0·8751
at 35 = 0·8723

compared with water at the same temperatures.

It is apparently formed from 4 mols. of œnanthaldehyde by the elimination of 3 mols. of water, according to the equation—

$$4C_7H_{14}O = C_{28}H_{50}O + 3OH_2.$$

The intermediate body, containing C_{21}, and standing between this body and the aldehyde previously described, could not be obtained pure ; it appears to be formed but only in very small quantities.

The principal products of the action of potash on œnanthaldehyde, so far as they have been studied, are, therefore, heptoic acid, the acid $C_{14}H_{26}O_2$, and the aldehydes $C_{14}H_{26}O$, and $C_{28}H_{50}O$.

Action of Zinc Chloride on Œnanthaldehyde.

These experiments were tried in the hope of getting a body corresponding to crotonic aldehyde, by the removal of the elements of water

from œnanthaldehyde. The action of zinc chloride on dry œnanthaldehyde is very violent. If the two are warmed together, two layers are quickly formed; the lower one being a solution of zinc chloride, and the upper one a dark brown oil, from which nothing definite could be obtained, as it decomposed on distillation. After numerous trials it was found that by modifying the process in the following way, the reaction was less complicated: œnanthaldehyde was shaken up with water until it was thoroughly saturated, separated from the excess of water, and warmed on a water-bath with a very small quantity of zinc chloride. In about 15 hours the action was finished. The product was then dissolved in a small quantity of ether, washed with water, dried, and fractioned. After the removal of the ether, it was distilled first *in vacuo*, as a quantity of high-boiling products were present. It was then further fractioned at the ordinary pressure. As soon as the unchanged œnanthaldehyde had distilled over, the thermometer rose rapidly to 260°, between which temperature and 300° the principal portion distilled over.

The residue was not distilled over; it contained probably the same high-boiling condensation-products as those obtained by the action of potash on œnanthaldehyde. The product boiling at 260—300°, on being fractioned, passed over principally at 276—280°, and judging from its boiling point was apparently the aldehyde $C_{14}H_{26}O$. This was proved to be the case by the determination of its specific gravity and analysis:—

I .. 0·1598 gram substance gave 0·1790 OH_2 and 0·4659 CO_2.
II .. 0·1527 „ „ 0·1710 „ 0·4479 „

	Found.		
	I.	II.	Theory, $C_{14}H_{26}O$.
C ..	79·54	79·97 per cent.	80·00 per cent.
H ..	12·44	12·44 „	12·38 „

The zinc chloride acts therefore as a dehydrating agent on œnanthaldehyde, as in the case of ordinary aldehyde—

$$2C_7H_{14}O = C_{14}H_{26}O + OH_2.$$

The yield of this aldehyde is about 30 per cent., whereas by the potash reaction it ranges from 70 to 83 per cent. of the theoretical quantity.

Action of Acetic Anhydride on the Aldehyde, $C_{14}H_{26}O$.

This experiment was tried in the hope of getting a diacetate from this body, as in the case of most aldehydes, according to the equation—

$$C_{13}H_{25}COH + \begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>\!O = C_{13}H_{25}CH\!<\!\begin{matrix}OOCCH_3\\OOCCH_3\end{matrix},$$

and of thus obtaining another proof of its being an aldehyde.

A mixture of this aldehyde and acetic anhydride was first boiled for three days in a flask connected with a reversed condenser; as it was found, however, that little or no reaction had taken place, it was then transferred to a sealed tube, and heated to about 180° for three days.

On distilling the product, and after the unchanged anhydride and acetic acid had distilled off, the thermometer rose rapidly to about 270°, when a small quantity of the unchanged aldehyde came over. The distillation was continued till the thermometer had reached 300°, and then the thick black residue was distilled under a pressure of 350 mm., when by far the largest quantity came over between 300—350°.

This portion was carefully fractioned under the same pressure. After repeating this operation two or three times, the principal portion distilled over between 330—340°, as a viscid light yellow oil. On heating this with alcoholic potash it turned dark brown, but no trace of acetic acid could be afterwards found combined with the alkali. The oil left after this treatment decomposed on distillation. It appeared therefore that the body was not an acetate. On analysis it gave the following numbers :—

I. 0·2353 gram substance gave 0·2600 OH_2 and 0·7242 CO_2.
II. 0·1975 „ „ 0·2219 „ 0·6069 „

	Found.		
	I.	II.	Theory, $C_{28}H_{50}O$.
C ..	83·94	83·81 per cent.	83·58 per cent.
H ..	12·28	12·48 „	12·43 „

This substance has therefore the composition $C_{28}H_{50}O$, and is doubtless identical with the one produced by the action of potash on œnanthaldehyde, as it possesses practically the same boiling point and specific gravity, and in fact resembles it in every respect. It appears therefore that the acetic anhydride acts as a dehydrating agent, extracting water from 2 mols. of $C_{14}H_{26}O$, being itself converted into acetic acid, according to the equation—

$$2C_{14}H_{26}O + (CH_3.CO)_2O = C_{28}H_{50}O + 2(CH_3.COOH).$$

In order, if possible, to get some idea of the constitution of this body, $C_{28}H_{50}O$, and of the nature of the groups contained in it, it was fused with excess of caustic potash in a silver crucible. In a short time the whole mass turned quite black and began to froth up and fume. After about five hours' heating it was allowed to cool, dissolved in water, and the oily matter removed with ether. The alkaline solution was then acidulated with hydrochloric acid, and the oily acid which separated taken up with ether. On distillation this acid boiled between

190° and 230°, and smelt like heptoic acid. It was converted into a potassium salt and then into a silver salt.

This salt gave the following numbers on analysis:—

0·3307 gram substance gave 0·1572 gram Ag = 47·53 per cent.

Calculated for $\left\{\begin{matrix}C_5H_{11}\\COOAg\end{matrix}\right.$ = 48·43 per cent.: $\left\{\begin{matrix}C_6H_{13}\\COOAg\end{matrix}\right.$ = 45·57 per cent.

It appeared therefore to be a mixture of hexoate and heptoate of silver. In order to see whether acetic acid, or any low-boiling acid soluble in water, had been formed, the original aqueous solution, which had been treated with ether, was distilled in steam. The distillate, however, was only very feebly acid, which was probably due to traces of heptoic acid. It appears, therefore, that only hexoic and heptoic acids are formed by the action of fused potash on $C_{28}H_{50}O$, and that, therefore, probably only hexyl and heptyl-groups are contained in it, which, it will be seen, is borne out by the oxidation-products of the body $C_{14}H_{26}O$, described further on.

It was attempted to distil *in vacuo* the oil which was separated from the potash salt, but it decomposed, and as only a few drops came over below 350°, it could not be examined.

Action of Nascent Hydrogen on the Aldehyde $C_{14}H_{26}O$.

As the body $C_{14}H_{26}O$ has the properties of an aldehyde, and at the same time is an unsaturated one, it was thought that it would be interesting to submit it to the action of nascent hydrogen. This was done in two ways—(I) in acetic acid solution; (II) in ethereal solution.

I. The aldehyde was dissolved in glacial acetic acid, and excess of sodium-amalgam slowly added, care being taken to keep the solution cool, in order to prevent, as far as possible, further condensation of the body $C_{14}H_{26}O$. Owing to the addition of considerable quantities of the amalgam, the sodium acetate formed rendered the liquid thick and unmanageable. It was found advisable therefore to precipitate the oil by means of water, wash, dry, &c., dissolve it again in acetic acid, and continue the treatment as before. When a considerable excess of amalgam had been used, the whole was diluted with water, and the oil taken up with ether. The ethereal solution, after being well washed in order to remove as much acetic acid as possible, was dried and fractioned. After the ether had distilled off, the principal quantity came over between 270—300°, and by repeated fractioning gave as the chief product a colourless oil boiling between 282—290°. An analysis of this substance gave the following numbers:—

0·1906 gram substance gave 0·2199 OH_2 and 0·5527 CO_2.

	Found.	Theory for $C_{14}H_{28}O$.
C	79·08 per cent.	79·25 per cent.
H	12·83 „	13·21 „

These numbers agree fairly well with those required by the formula $C_{14}H_{28}O$, which represents the aldehyde as having taken on H_2. As will be seen further on this product is an alcohol.

II. The treatment of the aldehyde in ethereal solution with nascent hydrogen was conducted in the following way:—

100 grams $C_{14}H_{26}O$ were dissolved in 400 grams ether, and the mixture poured upon water contained in a large flask, connected with a reversed condenser; small pieces of sodium were then very slowly added. The reaction was at first very violent, but became more controllable as the water got saturated with sodium hydrate. Before each addition of sodium, the mixture was well shaken, in order to dissolve out the sodium hydrate formed from the ethereal solution, which would otherwise cause the further condensation of the aldehyde $C_{14}H_{26}O$. The operation took about seven days, 50 grams of sodium being used. The ethereal solution was well washed, first with dilute hydrochloric acid, then with water, and afterwards dried over calcium chloride, and fractioned.

The principal part distilled over between 260—310°, but a considerable residue was left behind, which is referred to further on. In order to separate the new alcohol which is contained in this distillate from any unchanged aldehyde, it was found best to heat the fraction 260—310° with acetic anhydride in a sealed tube at 180° for three days. By this means the aldehyde is condensed to $C_{28}H_{50}O$, and the boiling point thereby considerably raised, whilst the new alcohol is at the same time converted into an acetate, which boils at about the same temperature as the alcohol itself, and is therefore very easy to obtain moderately pure by fractional distillation.

On distillation the largest portion of the product came over between 280—295°, and this on repeated fractioning gave as the principal product an oil boiling between 285—290°.

This oil, which is the acetate derived from the new alcohol, is a colourless, highly refractive liquid, having a pleasant smell. Its specific gravity is—

at 15° = 0·8680,
at 30 = 0·8597,
at 35 = 0·8568,

compared with water at the same temperatures.

On analysis it gave the following numbers:—

I. 0·2367 gram substance gave 0·2600 OH_2 and 0·6583 CO_2.
II. 0·2130 „ „ 0·2298 „ 0·5919 „

	Found. I.	Found. II.	Theory for $C_{14}H_{27}OC_2H_3O$.
C	75·85	75·78	75·59 per cent.
H	12·20	11·98	11·81 „

This acetate is readily decomposed by potash. A determination of the acetic acid produced by its saponification gave the following results:—

2·3442 grams substance saponified with dilute alcoholic potash gave 0·9256 gram potassium acetate = 24·16 per cent. $C_2H_4O_2$.
Calculated for $C_{14}H_{27}OC_2H_3O$ = 23·62 per cent.

To obtain the alcohol, the acetate was warmed with alcoholic potash, and completely saponified. Water was then added, and the alcohol taken up with ether. The ethereal solution after being dried was fractioned. When the ether had passed over, the thermometer rose rapidly, the largest quantity of the alcohol coming over between 278° and 290° as a colourless oil. On repeatedly fractioning this, it was obtained nearly pure, and boiling between 280—283°. It gave the following numbers on analysis, which agree satisfactorily with the formula $C_{14}H_{28}O$:—

I. 0·1723 gram substance gave 0·2021 OH_2 and 0·4999 CO_2.
II. 0·1950 „ „ 0·2354 „ 0·5643 „

	Found I.	Found II.	Calculated for $C_{14}H_{28}O$.
C	79·12	78·93 per cent.	79·25 per cent.
H	13·03	13·41 „	13·21 „

This alcohol is a colourless oil, having but little odour. It does not solidify at a temperature of −20°, and is not oxidised in contact with the air. It does not combine with acid sodium sulphite, nor reduce ammoniacal silver solution. The specific gravity of this alcohol is—

at 15° = 0·8520,
at 30 = 0·8444,
at 35 = 0·8418,

compared with water at the same temperatures.

Its formation from the aldehyde may be represented thus:—

$$C_{13}H_{25}COH + H_2 = C_{13}H_{25}CH_2OH.$$

The oily residue boiling above 300° left in the retort (produced by the action of nascent hydrogen on $C_{14}H_{26}O$ in ethereal solution) was

distilled in a vacuum, and then fractioned under a pressure of 300 mm. At first almost all the product came over between 310—350°, but after repeated fractioning the principal part boiled between 330—340°. It gave the following numbers on analysis:—

0·1424 gram substance gave 0·1634 OH_2 and 0·4370 CO_2.

	Found.	Theory for $C_{28}H_{50}O$.
C	83·69 per cent.	83·58 per cent.
H	12·74 „	12·43 „

These numbers agree with the formula for the body $C_{28}H_{50}O$, which is no doubt produced from the aldehyde $C_{14}H_{26}O$, by the condensing action of the sodium hydrate formed in the operation. Nascent hydrogen appears therefore to have no action on this body.

Action of Nascent Hydrogen on the Alcohol $C_{14}H_{28}O$.

In order to see whether it was possible to obtain a saturated alcohol of the formula $C_{14}H_{30}O$ by the continued action of nascent hydrogen on the unsaturated alcohol $C_{14}H_{28}O$, the following experiments were made:—

The alcohol was dissolved in ether, and treated with water and a large excess of sodium (in the same way as in the preparation of the alcohol itself). At the end of seven days the ethereal solution was separated from the water, and treated again with nascent hydrogen, using a 50 per cent. solution of acetic acid instead of ordinary water; the ethereal solution was then separated, well washed, dried, and after the ether had been distilled off, the oil fractioned. At first the greater part came over between 260° and 290°, but after fractioning two or three times, and last of all collecting between every 5°, the largest fraction obtained boiled between 270—275°.

On analysis this gave the following numbers:—

0·1612 gram substance gave 0·2028 OH_2 and 0·4669 CO_2.

	Found.	Theory for $C_{14}H_{30}O$.
C	78·99 per cent.	78·50 per cent.
H	13·98 „	14·02 „

It appears therefore that the saturated alcohol, $C_{14}H_{30}O$, is produced by the action of nascent hydrogen on $C_{14}H_{28}O$, though with difficulty, this unsaturated alcohol, as might be expected, being very slowly acted on by nascent hydrogen. This saturated alcohol obtained was not quite free from the unsaturated one, for on dissolving it in carbon bisulphide, cooling to −10°, and titrating with bromine, it took

up a small quantity without evolution of hydrobromic acid. The formation of this alcohol is expressed according to the equation—

$$C_{13}H_{25}CH_2OH + H_2 = C_{13}H_{27}CH_2OH.$$

A further description of this alcohol will be found in Part II of this investigation under the heading "Action of Nascent Hydrogen on the Aldehyde $C_{14}H_{28}O$."

In order to obtain an acetate of this alcohol, it was heated in a sealed tube with an excess of acetic anhydride for some time to 180—200°. On fractioning the product, almost all distilled over between 260—290°, and after repeating this operation two or three times, the principal portion obtained boiled at 275—280°. It gave the following results on analysis, agreeing with those required by the formula $C_{14}H_{29}O.C_2H_3O$:—

0·1320 gram substance gave 0·1501 gram OH_2 and 0·3643 CO_2.

	Found.	Calculated for $C_{14}H_{29}OC_2H_3O$.
C	75·27 per cent.	75·00 per cent.
H	12·63 „	12·50 „

Oxidation of $C_{13}H_{25}COH$.

In order if possible to obtain some definite clue as to the constitution of this aldehyde, several experiments were made with different oxidising agents.

(1.) *Oxidation with Chromic Acid.*

50 grams of $C_{14}H_{26}O$ were dissolved in glacial acetic acid, and treated with twice its weight of chromic acid dissolved in glacial acetic acid. The reaction was very violent, and the oxidising mixture had to be added very slowly, the product being well cooled after each addition. Every time the solution of chromic acid was run in, the liquid frothed up, carbonic anhydride being given off in large quantities. As soon as all the chromic acid solution had been added, the product was heated on a water-bath for two hours, to ensure the oxidation being as complete as possible. A considerable quantity of water was then added, and the whole shaken up with ether three or four times. It was afterwards found best to distil off the volatile products from the green liquid by means of steam, and then to treat the distillate with ether. The ethereal solution was separated, washed several times with water, in order to remove as much acetic acid as possible, and the acids contained in it were separated from any neutral bodies formed in the reaction, by treatment with a dilute solution of potash. The potash

solution was then separated from the ethereal, acidulated with hydrochloric acid, and the acids thus liberated taken up with ether. The ethereal solution was well washed, dried, and fractioned. After the ether had distilled off, almost all the remaining products came over between 190—230°, but all attempts to get substances with a constant boiling point were in vain. The whole was therefore made into a potassium compound by dissolving it in a solution of potassium carbonate and evaporating it to dryness. The saline product was then repeatedly extracted with absolute alcohol, to free it from potassium carbonate, and the solution evaporated to dryness. After repeating this purification with alcohol, the salt was dissolved in water, and a silver salt prepared from it by precipitation with nitrate of silver. The salt thus obtained, after being well washed and dried, was analysed, but no good results were obtained, the numbers always coming between those calculated for heptoate and hexoate of silver. Several attempts were made to crystallise the salt from water and alcohol, but without success.

As it appeared possible that both acids might be present, the oxidation was again repeated, with 100 grams aldehyde, as the yield of acid is very small, most of the aldehyde being oxidised to carbonic anhydride. The acids obtained in this operation were then fractioned with great care, and separated principally into two quantities, boiling at 203—207° and 218—228°. Each of these was separately converted into potassium salts, dried, and purified as before with absolute alcohol, and after repeating the purification, dissolved in water. In order to obtain silver salts as pure as possible, each product was fractionally precipitated with silver nitrate into five quantities. Silver determinations were then made with the 10 fractions, and these showed without doubt that the acids found consist of a mixture of hexoic and heptoic acids.

The fractions which gave the best silver determinations were completely analysed. Of those prepared from the potassium salt of the acid (b. p. 203—207°), fraction III gave the best results; and from the potassium salt of the acid (b. p. 218—228°) fraction II. No. III (203—207°) gave the following results on analysis:—

I. 0·2098 substance gave 0·2463 CO_2, 0·0924 OH_2, 0·1019 Ag.
II. 0·2016 „ „ 0·2366 „ 0·0900 „ 0·0978 „

	Found.		Calculated for $C_5H_{11}COOAg$.
	I.	II	
C	32·17	32·01 per cent.	32·28 per cent.
H	4·89	4·96 „	4·93 „
Ag	48·57	48·51 „	48·43 „

There can therefore be no doubt it consisted of hexoate of silver.

No. II (218—228°) fraction gave on analysis the following numbers:—

I. 0·2200 substance gave 0·1102 OH_2, 0·2855 CO_2, and 0·1008 Ag.
II. 0·2163 „ „ 0·1057 „ 0·2796 „ 0·0991 „

	Found. I.	Found. II.		Calculated for $C_6H_{13}COOAg$.
C	35·38	35·25	per cent.	35·44 per cent.
H	5·56	5·43	„	5·48 „
Ag	45·81	45·82	„	45·57 „

It was therefore without doubt heptoate of silver.

The aldehyde $C_{13}H_{25}COH$ splits up therefore on oxidation into carbonic anhydride, and heptoic and hexoic acids, according to the equation—

$$C_{14}H_{26}O + O_5 = C_6H_{13}COOH + C_5H_{11}COOH + CO_2.$$

The ethereal solution of the neutral oils from these oxidation experiments was then repeatedly fractioned, but no constant boiling point could be obtained. The oil began to boil at 250°, but mostly distilled above 360°. I hope at some future time to be able to study this subject in a more exhaustive way.

(2.) *Oxidation by the Air.*

As it seemed probable that by gentle oxidation, such as direct absorption of oxygen from the air, the acid of the formula $C_{14}H_{26}O_2$ would be formed, identical with that obtained by the action of potash, both on œnanthaldehyde and $C_{14}H_{26}O$, the following experiments were made:—First, a considerable quantity of the aldehyde was exposed to the air in flat dishes for three weeks. In order to hasten the oxidation, the product was gently heated by placing the dishes on a water-bath, and well stirred every day. In a few days it became very thick and slightly yellow, and appeared inclined to become solid on the surface. A second experiment was made by saturating filter-paper with the oil, and then hanging it up in the air for a week to oxidise. The oil was then extracted by digesting with ether. In both cases the oil was afterwards dissolved in ether, and the acids formed separated from the unchanged or neutral oils by shaking with dilute potash-solution. The potash-solutions were treated with ether two or three times, to ensure their freedom from oil, and after being carefully neutralised with sulphuric acid, evaporated to dryness. The whole mass was then extracted several times with absolute alcohol, and again evaporated to dryness. The organic potassium salts were acidulated

with dilute hydrochloric acid, and treated with ether, the ethereal solution then separated, well washed, dried, and the ether distilled off.

The quantity of acid left was very small, and smelt strongly of heptoic acid. It was carefully fractioned, when by far the largest quantity distilled over between 200—230°. There was only a very small quantity of a high-boiling acid left behind, which was most probably the acid $C_{14}H_{26}O_2$, but it could not be obtained pure enough for analysis. The fraction 200—230° was made into the potassium compound in the usual way, and then precipitated with nitrate of silver; the silver salt gave the following numbers on analysis :—

0·2219 gram substance gave 0·1072 OH_2, 0·2756 CO, 0·1030 Ag.

	Found.	Calculated $\left\{\begin{matrix}C_5H_{11}\\COOAg\end{matrix}\right.$	$\left\{\begin{matrix}C_6H_{13}\\COOAg\end{matrix}\right.$
C	33·87 per cent.	32·28 per cent.	35·44 per cent.
H	5·37 „	4·93 „	5·48 „

It was therefore undoubtedly a mixture of hexoate and heptoate of silver. The acid $C_{14}H_{26}O_2$ may probably have been first formed, but being very unstable rapidly oxidised under the influence of the air and potash into heptoic and hexoic acids. The ethereal solution of the neutral oils, which was separated from the acids by shaking with potash, was examined. The oils it contained began to boil at 250°, but the principal part passed over above 300°. Several of the fractions were analysed, but no definite results were obtained; there appeared, however, to be no unchanged substance left.

(3.) *Oxidation with Silver Oxide.*

As it seemed possible that the acid $C_{14}H_{26}O_2$ might perhaps be obtained in larger quantities by the oxidation of the aldehyde $C_{14}H_{26}O$ with a gentle oxidising agent, such as silver oxide, several experiments were made in this direction. The following method was tried :—About 20 grams of $C_{14}H_{26}O$ were shaken up with freshly precipitated silver oxide and water in a flask connected with a reversed condenser. The oil quickly adheres to the oxide of silver, and falls to the bottom of the flask, when the greater quantity of the water can be poured off. The mixture was then heated to boiling in a bath of a concentrated solution of carbonate of soda for about 24 hours; at the end of this time all the silver was reduced. Dilute hydrochloric acid was then added, to decompose any silver salts formed, and the whole well shaken up with ether several times, to extract the oil from the precipitated silver. The acid products were separated from the ethereal solution of the oil as before by shaking with dilute potash. The potash-solution was acidulated with dilute hydrochloric acid, treated with ether, and

the ethereal solution separated, dried, and fractioned. As soon as the ether had distilled off, nearly all the residue boiled between 190—230°. The residue, consisting of high-boiling acid, was again so small that it was found impossible to purify it. The fraction 190—230° was turned into the potash compounds, and then precipitated with nitrate of silver; a silver determination of the silver salt thus made gave the following result:—

0·2320 gram substance gave 0·1087 Ag = 46·85 per cent.
Calculated for $C_6H_{13}COOAg$ = 45·57; $C_5H_{11}COOAg$ = 48·43.

It was therefore as before a mixture of hexoic and heptoic acids. The unoxidised oil gave also the same curious results as those obtained when the other oxidising agents were used.

(4.) *Action of Potash on the Aldehyde* $C_{14}H_{26}O$.

As the body $C_{14}H_{26}O$ is an aldehyde, it was thought that it would be interesting to see what the further action of potash on it would be, more especially as it appeared probable that by this means some clue might be obtained to the constitution of the higher condensation-products of œnanthaldehyde. Alcoholic potash acts very readily on this aldehyde, when it is gently heated with it, the whole becoming black, a considerable quantity of a potash salt being at the same time formed, but the oils in this case are very uninviting, and difficult to purify. If the potassium salts are to be examined, it is best to act on the aldehyde with moderately strong alcoholic potash, and to warm the mixture. In examining the oils, however, the following method was found to give the best results:—200 grams of the aldehyde were dissolved in 500 grams alcohol, and 20 grams of a concentrated solution of potassium hydrate in alcohol added in small quantities every day for about six weeks, the whole being well shaken after each addition. By this means the condensation and other changes take place slowly, and there are also less tarry products formed. The mixture, after standing for another two weeks, was diluted with water, and the oil taken up with ether. The aqueous potash-solution was then acidulated with dilute hydrochloric acid, and the liberated acids which it contained removed with ether. The ethereal solution was dried and fractioned. The greater part distilled over between 210—230°; there was a small residue left. The fraction 210—230° was made into potash salt, and then into a silver salt. A silver estimation gave the following result:—

0·7520 gram substance gave 0·3433 gram Ag = 45·65 per cent.
Calculated for $C_6H_{13}COO$ Ag = 45·57 per cent.

It was therefore without doubt heptoate of silver. The residue,

which boiled above 230°, was transferred to a small retort, and two or three times very carefully fractioned under a pressure of 250 mm. The largest fraction obtained, boiled between 275—280°. The quantity was, however, very small—about 2 grams. An analysis of it gave the following results :—

0·1469 gram substance gave 0·1520 gram OH_2 and 0·3969 CO_2.

	Found.	Calculated $C_{14}H_{26}O_2$.
C	74·24 per cent.	74·33 per cent.
H	11·49 „	11·50 „

This body has therefore the formula $C_{14}H_{26}O_2$, and is without doubt the same acid as that which was obtained by the action of alcoholic potash on œnanthaldehyde. It is a light yellow oil, possessing but little odour, and does not solidify in a freezing mixture. It dissolves without much difficulty in dilute ammonia. On standing over sulphuric acid, the ammonia salt quickly deposits an oil which is probably the amide of the acid. A solution of the ammonia salt was prepared by dissolving the acid in dilute ammonia, nearly neutralising with dilute nitric acid, and then allowing the salt to stand for a short time over sulphuric acid. It was then filtered through a wet filter-paper, and the following salts prepared :—

The *silver salt* is precipitated on adding silver nitrate as a white flocculent precipitate, which is instantly decomposed on boiling with water.

The *barium salt*, precipitated by adding barium chloride, is a white amorphous precipitate, insoluble in water, but apparently slightly soluble in alcohol.

The *calcium salt* resembles in every respect the barium salt.

The *copper salt* is precipitated on adding sulphate of copper, as a beautiful emerald-green precipitate, which is insoluble in water and becomes black on boiling.

Unfortunately, the amount of acid procured has been so small that it has not been found possible to prepare enough of its salts for analysis. The potassium salt is difficult to prepare, a soap being formed on treating the acid with a solution of potassium carbonate.

The ethereal solution containing the condensed aldehyde and other neutral bodies was next washed, dried over calcium chloride, and fractioned. After the ether had been slowly distilled off, about 3 grams of oil came over between 100° and 200°; the thermometer then rose rapidly to 250°, between which temperature and 300° a considerable quantity of product distilled over. By far the largest quantity remained behind in the retort above 300°, and was reserved for distillation in a vacuum. The fraction 100—200° was fractioned, and

mostly came over between 170—180°. On analysis it gave the following results:—

0·1145 gram substance gave 0·1394 gram OH_2 and 0·3050 CO_2.

	Found.	Calculated for $C_6H_{13}CH_2OH$.
C	72·64 per cent.	72·41 per cent.
H	13·52 „	13·79 „

It was therefore heptyl alcohol. It is formed in very small quantity, only about 1 gram boiling between 170—180° being obtained.

The fraction 250—300° was then heated in a sealed tube with excess of acetic anhydride at 180° for three days, in order to modify any unchanged aldehyde. On fractioning, from 5—10 grams distilled over below 300°. In order to be certain that none of the aldehyde $C_{14}H_{26}O$ was present, this fraction was again heated with acetic anhydride to 200° for two days, and refractioned. The principal quantity distilled over between 270—295°, and after further fractioning, gave from 2—3 grams of an oil which boiled between 280—290°. Two analyses of these gave the following results:—

I. 0·1210 gram substance gave 0·1293 OH_2 and 0·3386 CO_2.
II. 0·1114 „ „ 0·1164 „ 0·3124 „

	Found. I.	Found. II.	Theory for $C_{14}H_{27}OC_2H_3O$.
C	76·31	76·48 per cent.	75·59 per cent.
H	11·87	11·61 „	11·81 „

These numbers agree fairly with the formula $C_{14}H_{27}O.C_2H_3O$, which is that of the acetate of the alcohol $C_{14}H_{28}O$; but owing to the smallness of the quantity, it was found impossible to get it in a purer condition. In order, if possible, to confirm this result by preparing the alcohol, the alcoholic potash reaction was tried again, 150 grams of the aldehyde $C_{14}H_{26}O$ being used, the mixture being warmed for two days. The oil was then fractioned as before, and the fraction 250—300° treated with acetic anhydride. The acetate was then saponified with alcoholic potash, and the resulting alcohol repeatedly fractioned. In this way a considerable quantity was obtained boiling between 280—290°, and gave the following result on analysis:—

0·1088 gram substance gave 0·1304 gram OH_2 and 0·3176 CO_2.

	Found.	Theory for $C_{14}H_{28}O$.
C	79·61 per cent.	79·25 per cent.
H	13·31 „	13·21 „

It is therefore evident that this alcohol is formed in this reaction,

although in but small quantities. The residue of the original condensed product which boiled above 300° was, without doubt, the principal product of the reaction, and as it was very black, it was first distilled under reduced pressure. A considerable quantity came over between 280—360° under 250 mm. pressure. This was several times fractioned under 350 mm. pressure; the principal quantity obtained boiled between 335—340°. It was a light yellow oil, which distilled without the least decomposition in a vacuum. On analysis it gave the following numbers:—

0·1235 gram substance gave 0·1374 OH_2 and 0·3770 CO_2.

	Found.	Theory for $C_{28}H_{50}O$.
C	83·25 per cent.	83·58 per cent.
H	12·36 „	12·43 „

It was therefore the compound $C_{28}H_{50}O$ previously described. The products of the action of alcoholic potash on $C_{14}H_{26}O$ are therefore: $C_{28}H_{50}O$, $C_{14}H_{28}O$, $C_6H_{13}CH_2OH$, and the acids $C_6H_{13}COOH$ and $C_{14}H_{26}O_2$.

The body $C_{28}H_{50}O$ is evidently produced by the condensation of two molecules of the aldehyde $C_{14}H_{26}O$—in exactly the same way as the aldehyde $C_{14}H_{26}O$ itself is formed from œnanthaldehyde—according to the equation—

$$2C_{14}H_{26}O = C_{28}H_{50}O + OH_2.$$

Heptoic acid and heptyl alcohol are probably formed according to the equation—

$$C_{14}H_{26}O + KOH + OH_2 = \left\{\begin{matrix} C_6H_{13} \\ COOK \end{matrix}\right. + \left\{\begin{matrix} C_6H_{13} \\ CH_2OH. \end{matrix}\right.$$

The formation of the acid $C_{14}H_{26}O_2$ and the alcohol $C_{14}H_{29}O$ may also be represented thus:

$$2C_{14}H_{26}O + KOH = C_{14}H_{25}OOK + C_{14}H_{28}O.$$

In these two last equations the potash evidently exerts an oxidising as well as a reducing action, analogous to the action of the same agent on the aromatic aldehydes, as for example in the case of benzaldehyde, which is converted by it into potassic benzoate and benzyl alcohol:—

$$2C_6H_5COH + KOH = C_6H_5COOK + C_6H_5CH_2OH.$$

In order to more thoroughly examine these secondary reactions, it would be necessary to work with very large quantities of the aldehyde $C_{14}H_{26}O$.

Theoretical Remarks.

As the body $C_{14}H_{26}O$ on oxidation splits up into heptoic and

hexoic acids, and is an aldehyde, it can only have the following constitution :—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH \\ \qquad\qquad\qquad\qquad\qquad\quad \| \\ CH_3.CH_2.CH_2.CH_2.CH_2.C.COH. \end{array}$$

It may be called hexyl-pentyl-acryl aldehyde, and is formed from two molecules of œnanthaldehyde, according to the equation—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH \quad O \\ \qquad\qquad\qquad\qquad\qquad\quad \diagdown\!\diagup \quad H_2 \\ CH_3.CH_2.CH_2.CH_2.CH_2.C.COH \end{array} =$$

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH \\ \qquad\qquad\qquad\qquad\qquad\quad \| \\ CH_3.CH_2.CH_2.CH_2.CH_2.C.COH \end{array} + OH_2.$$

In order to show it was unsaturated as indicated by the equation, 51·25 grams of the aldehyde $C_{14}H_{26}O$ were dissolved in bisulphide of carbon cooled down to $-10°$, and titrated with dry bromine. It took up 39·10 grams bromine (traces of hydrobromic acid only being produced) = 76·32 per cent.; calculated quantity for $C_{14}H_{26}O + Br_2$ is = 76·66 per cent. In this case there is no doubt that a body of the following formula is formed :—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CHBr \\ \qquad\qquad\qquad\qquad\qquad\quad \cdot \\ CH_3.CH_2.CH_2.CH_2.CH_2.CBr.COH \end{array}$$

It is, however, impossible to isolate this product; for as soon as the solution in carbon bisulphide attains a temperature of 30°, hydrobromic acid begins to come off, and the whole turns black. The oxidation of the aldehyde $C_{14}H_{26}O$ takes place apparently according to the following equation :—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH \\ \qquad\qquad\qquad\qquad\qquad\quad \| \\ CH_3.CH_2.CH_2.CH_2.CH_2.C.COH \end{array} + O_5 =$$

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2CH_2.CH_2.COOH \\ + CH_3.CH_2.CH_2.CH_2.CH_2.COOH \end{array} + CO_2.$$

As the body $C_{28}H_{50}O$ is produced by the action of potash or acetic anhydride on $C_{14}H_{26}O$ with separation of water, it follows that it must be formed from two molecules of $C_{14}H_{26}O$. By melting with potash, it gives only the two acids: heptoic and hexoic acids. The following formula will therefore represent its constitution :—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad CH_3.CH_2.CH_2.CH_2.CH_2.C\,.\,CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\quad CH_3.CH_2.CH_2.CH_2.CH_2.C\,.\,CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\quad CH_3.CH_2.CH_2.CH_2.CH_2.C.COH. \end{array}$$

Its formation from two molecules of $C_{14}H_{26}O$ would then take place according to the equation:—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad CH_3.CH_2.CH_2.CH_3.CH_2.C.CH \quad O \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \quad H_2 \\ \qquad\qquad\qquad CH_3.CH_2.CH_2.CH_2.CH_2.C.CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad CH_3.CH_2.CH_2.CH_2.CH_2.C.COH \\ = C_{28}H_{50}O + OH_2 \end{array}$$

If the constitution given for the aldehyde $C_{14}H_{26}O$ be correct, the unsaturated alcohol $C_{14}H_{28}O$, which is formed from it by the action of nascent hydrogen, may be represented thus—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad CH_3.CH_2.CH_2.CH_2.CH_2.C.CH_2OH, \end{array}$$

and the saturated alcohol, being formed by the action of nascent hydrogen on the unsaturated alcohol, will therefore have the following constitution:—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad CH_3.CH_2.CH_2.CH_2.CH_2.CH.CH_2OH, \end{array}$$

and is therefore β-heptyl-heptyl alcohol, or heptyl-pentyl-ethyl alcohol.

And finally the acid $C_{14}H_{26}O_2$ will have the constitution

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad CH_3.CH_2.CH_2.CH_2.CH_2.C.COOH, \end{array}$$

and is therefore hexyl-pentyl-acrylic acid.

IX.—*Condensation-products of Œnanthaldehyde* (Part II).

By W. H. Perkin, Jun., Ph.D.

Action of Nascent Hydrogen on Œnanthaldehyde.

In the preparation of heptyl alcohol by the action of nascent hydrogen on œnanthaldehyde, there is always a considerable quantity of a high-boiling bye-product formed, which often amounts to 20 per cent. of the œnanthaldehyde used. This remains in the retort, on distilling off the heptyl alcohol, as a thick brown oil, which, however, does not seem to have been investigated. As it was probable that these oils were simply condensation-products, produced by the dehydrating action of the agents used, and possibly acted on by the nascent hydrogen; it was thought that they might yield interesting results upon examination. The inquiry was divided into two parts: (1), action of nascent hydrogen on œnanthaldehyde in acid solution; (2), in ethereal solution.

(1.) *Action of Nascent Hydrogen on Œnanthaldehyde in Acetic Acid Solution.*

The operations were conducted in the same manner as described in Part I, in the section on the action of nascent hydrogen in acid solution on the aldehyde $C_{14}H_{26}O$. It is practically the same as that employed by C. F. Cross (*Jour. Chem. Soc.*, **32**, 123) for the preparation of heptyl alcohol. 200 grams of œnanthaldehyde were used in each operation, and about twice as much sodium amalgam as theoretically required for the formation of heptyl alcohol.

At the end of the reaction water was added, and the oil, after being washed, was boiled with a dilute solution of potash, in order to decompose acetates, which are always formed. It was then washed, dried, and distilled under reduced pressure (350 mm.), until the temperature reached 300°. The residue was not examined. The distillate was fractioned under ordinary pressure. The principal quantity, consisting of heptyl alcohol and a small quantity of unchanged œnanthaldehyde, came over below 200°; the thermometer then rose rapidly to 240°, between which temperature and 300° a large amount of product distilled over. This last quantity was repeatedly rectified, when three fractions were obtained, boiling between 270—275°, 275—280°, and 280—283°, all of about the same size. The analyses of these gave numbers which always came between those calculated for the alde-

hyde $C_{14}H_{26}O$, and the alcohol $C_{14}H_{28}O$, so that it appeared very probable that both were present. In order to separate them the fractions between 265—285° were heated in sealed tubes with excess of acetic anhydride at 180—200° for four days, and then distilled. After the acetic acid and excess of anhydride had passed over, a considerable quantity of oil was obtained boiling between 270—300°. There was, however, a dark brown residue left, which would seem to show that, as was anticipated, some aldehyde, such as $C_{14}H_{26}O$, was previously present, and had been condensed by the action of the acetic anhydride.

The oil distilling between 270—300° was then repeatedly fractioned, and at last gave a product which boiled pretty steadily between 280—285°. It was a colourless, highly refracting oil, possessing an agreeable odour. The analysis gave the following numbers:—

I. 0·1860 gram substance gave 0·1992 gram OH_2 and 0·5170 gram CO_2.

II. 0·2167 gram substance gave 0·2302 gram OH_2 and 0·6030 gram CO_2.

	Found.		Calculated $C_{16}H_{30}O_2$ = $C_{14}H_{27}OC_2H_3O$.
	I.	II.	
C.....	75·81	75·89 per cent.	75·59 per cent.
H	11·90	11·80 „	11·81 „

This was therefore the acetate derived from the alcohol $C_{14}H_{28}O$. As this substance, from its composition, should be an unsaturated body, it was dissolved in carbon disulphide, cooled down to −10°, and titrated with bromine. The colour of the bromine disappeared instantaneously without evolution of hydrobromic acid. A quantitative experiment gave the following numbers:—

2·2355 grams substance took up, without evolution of hydrobromic acid, 1·3477 gram bromine = 60·3 per cent.

Calculated for $C_{16}H_{30}O_2 + Br_2$ = 62·9 per cent.

Attempts were made to isolate the bromine addition-product, but the body decomposes on distilling off the carbon disulphide, giving off hydrobromic acid.

This acetate was saponified by boiling with alcoholic potash. On distilling off the alcohol and adding water to the residue, the alcohol $C_{14}H_{28}O$ separates as an oil. This was taken up with ether, and the ethereal solution distilled. After a few fractional distillations the principal quantity came over as a colourless oil boiling at 280—283°. Analysis gave the following result:—

0·1494 gram substance gave 0·1777 OH_2 and 0·4340 CO_2.

	Found.	Calculated $C_{13}H_{25}CH_2OH$.
C	79·23 per cent.	79·25 per cent.
H.....	13·22 „	13·21 „

There can be no doubt that this alcohol and the acetate from which it was separated are the same bodies as those described in Part I, p. 55, as the properties of the two so closely agree. The formation of this alcohol from œnanthaldehyde is probably due to the dehydrating action of the glacial acetic acid and sodium acetate, formed in the reaction, first producing the aldehyde $C_{14}H_{26}O$, a part of which is then acted on by nascent hydrogen, yielding this product. It is practically impossible to separate the aldehyde $C_{14}H_{26}O$ from the alcohol $C_{14}H_{28}O$ by fractional distillation, but the treatment with acetic anhydride forms an easy way of separating them, as shown in Part I.

The products of the action of nascent hydrogen in acid solution, as far as they have been examined, are therefore, heptyl alcohol, probably the aldehyde $C_{14}H_{26}O$, and the alcohol $C_{14}H_{25}O$.

(2.) *Action of Nascent Hydrogen on Œnanthaldehyde in Ethereal Solution.*

This operation was conducted in the same way as that described in Part I, p. 54, where the treatment of an ethereal solution of the aldehyde, $C_{14}H_{26}O$, is described. 450 grams of œnanthaldehyde dissolved in about $1\frac{1}{2}$ to 2 litres of ether, and from 200 to 210 grams of sodium, were used in each experiment, which required from four to five days for completion.

The ethereal was separated from the aqueous solution, well washed, first with dilute hydrochloric acid and then with water, and dried over calcium chloride. The examination of the aqueous solution showed that it contained an oily acid boiling between 221—225°; it gave the following numbers on analysis:—

0·2714 gram substance gave 0·2631 gram OH_2 and 0·6400 gram CO_2.

	Found.	Calculated for $C_6H_{13}COOH$.
C	64·31 per cent.	64·61 per cent.
H.....	10·77 „	10·77 „

It was therefore heptoic acid.

The ethereal solution, containing the neutral oils, was next examined. After the ether had been distilled off, the oil was fractioned in a stream of carbonic anhydride.

It began to boil at 150°, between which temperature and 200° a considerable quantity distilled over, consisting of a mixture of heptyl

alcohol and unchanged œnanthaldehyde. The thermometer then rose rapidly to 250°, a large quantity coming over between 250—300°. The residue was reserved for distillation *in vacuo*, and is referred to further on. The portion boiling between 250—300° was several times carefully fractioned in a stream of carbonic anhydride, as the oils oxidise in the air. It was found that when cooled down to 0° all the fractions from 255—280° deposited crystals, some becoming almost solid. In order to obtain this solid product in a pure state, the various fractions were cooled down to −20° in a mixture of ice and hydrochloric acid, and the oil then filtered off from the crystals as quickly as possible, by means of a vacuum pump. They were then quickly pressed between filter-paper at as low a temperature as possible, and further purified by crystallisation from ether, in which they are very soluble; on allowing the solution to evaporate spontaneously, large transparent crystals, with a beautiful lustre, were deposited. These were filtered off from the ethereal solution, and placed over sulphuric acid in an atmosphere of CO_2 for some time. The following analyses were made from several preparations :—

I.	0·1693	gram	substance	gave	0·1977	OH_2 and 0·4939	CO_2.
II.	0·2333	,,	,,	,,	0·2760	,, 0·6755	,,
III.	0·2426	,,	,,	,,	0·2846	,, 0·7015	,,
IV.	0·1543	,,	,,	,,	0·1818	,, 0·4474	,,
V.	0·1565	,,	,,	,,	0·1872	,, 0·4543	,,
VI.	0·1985	,,	,,	,,	0·2355	,, 0·5741	,,
VII.	0·1308	,,	,,	,,	0·1561	,, 0·3795	,,
VIII.	0·1467	,,	,,	,,	0·1770	,, 0·4251	,,

Found.

	I.	II.	III.	IV.	V.	VI.
C.....	79·56	78 96	78·86	79·07	79·17	78·88
H.....	12·97	13·14	13·03	13·09	13·29	13·18

Found.

	VII.	VIII.	Mean.	Theory $C_{14}H_{28}O$.
C.....	79·13	79·01	79·09 per cent.	79·25 per cent.
H.....	13·26	13·40	13·19 ,,	13·21 ,,

This substance therefore has the formula $C_{14}H_{28}O$. It is a beautiful body, crystallising in plates which melt at 29·5°. It boils without the least decomposition at 266—268°. It is easily soluble in carbon disulphide, ether, alcohol, petroleum ether, and chloroform. The solution in carbon disulphide, if cooled down to −10°, does not take up bromine, it therefore appears to be a saturated body. It combines very slowly with hydrogen sodium sulphite, so that, after standing for six months with a concentrated solution of the latter body, it had not quite ceased depositing crystals. The amount of the compound obtained was unfortunately too small for analysis. This body also reduces an ammoniacal silver solution, and oxidises, when left in contact with the air, but only very slowly when in the solid state. From these properties it appears to be an aldehyde. Heated with acetic anhydride for four days in a sealed tube at 180°, it did not form an acetate. Acetic anhydride appears to act on it very slowly, as on fractioning the product there was only a very small residue left in the retort above 280°. The specific gravity of this aldehyde in the fused state is—

at 30° = 0·8274
at 35 = 0·8258

compared with water at the same temperatures. Its formation from œnanthaldehyde may be expressed by the following equation :—

$$2C_7H_{14}O + H_2 = C_{14}H_{28}O + OH_2.$$

The residue left in the retort above 310°, after distilling off the aldehyde just described, was very thick and black, and was therefore first distilled *in vacuo*, and then fractioned under a pressure of 300 mm. By the first distillation a considerable quantity of an almost colourless oil distilled over between 310—350°. On repeatedly fractioning under the same pressure, two principal products were obtained, boiling between 315—320° and 320—325°, of which the first was the larger. Analyses of these gave the following results :—

I. (320—325°) 0·2466 gram substance gave 0·2882 OH_2 and 0·7347 CO_2.
II. (315—320°) 0·1782 gram substance gave 0·2084 OH_2 and 0·5332 CO_2.
III. (315—320°) 0·1480 gram substance gave 0·1734 OH_2 and 0·4432 CO_2.
IV. (315—320°) 0·2159 gram substance gave 0·2540 CO_2 and 0·6466 CO_2.

	Found.				
	I.	II.	III.	IV.	Theory $C_{21}H_{40}O$.
C	81·26	81·60	81·67	81·66 per cent.	81·82 per cent.
H	12·99	12·99	13·02	13·07 ,,	12·99 ,,

This body has therefore the formula $C_{21}H_{40}O$. It is a slightly yellow, very thick oil, which does not solidify at $-10°$. It reduces ammoniacal silver solution, but does not appear to combine with hydrogen sodium sulphite. Heated with potash it becomes thick and black, a small quantity of a potash salt being formed. Boiling with dilute sulphuric acid also decomposes it. In order to see if it were unsaturated, it was dissolved in carbon disulphide, cooled down to -10, and titrated with bromine. The colour of the bromine disappeared instantly. A quantitative experiment gave the following result:—

20·65 grams dissolved in carbon disulphide, took up 10·8 grams bromine without the evolution of hydrobromic acid = 52·3 per cent.

Calculated for $C_{21}H_{40}O + Br_2$ = 51·9 per cent.

It appears therefore to be an unsaturated body. Its formation from œnanthaldehyde may be represented by the following equation:—

$$3C_7H_{14}O + H_2 = C_{21}H_{40}O + 2OH_2.$$

Its specific gravity was found to be:—

at 15° = 0·8744
at 30 = 0·8665
at 35 = 0·8637

compared with water at the same temperatures.

The yield of this body is from 5 to 10 per cent. of the œnanthaldehyde used.

The residue in the retort, boiling above 350° *in vacuo*, became solid on cooling. On extracting with ether a white solid body remained behind, which dissolved on boiling with water. On cooling, needles of calcium heptoate crystallised out. A calcium estimation gave 13·44 Ca. Calculated for $(C_6H_{13}COO)_2Ca$ = 13·43 per cent. Ca. The presence of this salt is probably due to the fact that the crude oil was in the first place dried over calcium chloride, which is a little soluble in the oil, and that, at the high temperature employed in the following distillations, it was converted into calcic heptoate. The products of the action of nascent hydrogen in alkaline solution on œnanthaldehyde, as far as they have been examined, are therefore:—

Heptyl alcohol: heptoic acid: the solid aldehyde $C_{14}H_{28}O$: and the body $C_{21}H_{40}O$.

Oxidation of the Aldehyde $C_{14}H_{28}O$.

In order to obtain some idea as to the constitution of this aldehyde, $C_{14}H_{28}O$, and of the nature of the groups contained in it, several oxidation experiments were made, much in the same way as in the case of the aldehyde $C_{14}H_{28}O$, described in Part I. The aldehyde $C_{14}H_{28}O$ was dissolved in glacial acetic acid, and one and a-half times its weight of chromic acid dissolved in glacial acetic acid slowly added, the product being well cooled after each addition. The action is very energetic, large quantities of carbonic anhydride being given off. As soon as all the chromic acid had been added, the product was heated for two hours on a water-bath to complete the oxidation. The product was treated as in the analogous experiments in Part I. The acids obtained came over between 190° and 230°, and the liquid thus obtained was separated by further distillation into two fractions boiling between 195—210° and 210—230°. Each of these was converted into a potassium compound and then fractionally precipitated with nitrate of silver into five fractions. Silver estimations were made in each of these precipitates.

The results showed clearly that a mixture of hexoate and heptoate of silver was present. The silver salts which gave the best results were fully analysed, and gave the following numbers. Of that from the potassium salt of the acid (195—210°), fractions IV and V were analysed, with the following results:—

I. 0·2202 gram substance gave 0·1000 OH_2, 0·2649 CO_2, and 0·1052 Ag.

II. 0·2479 gram substance gave 0·1121 OH_2, 0·2939 CO_2, and 0·1202 Ag.

III. 0·2267 gram substance gave 0·1040 OH_2, 0·2742 CO_2, and 0·1083 Ag.

	Found.				Theory for $\left\{\begin{matrix}C_5H_{11}\\COOAg\end{matrix}\right.$
	I.	II.	III.		
C	32·81	32·33	32·97	per cent.	32·28 per cent.
H	5·05	5·02	5·10	,,	4·93 ,,
Ag ..	47·77	48·48	47·77	,,	48·43 ,,

It was, therefore, without doubt, hexoate of silver.

Of that from the potassium salt of the acid 218—230° fractions II and III were analysed with the following results:—

I. 0·2435 gram substance gave 0·1215 OH_2, 0·3174 CO_2, and 0·1112 Ag.

II. 0·1533 gram substance gave 0·0759 OH_2, 0·1975 CO_2, and 0·0702 Ag.

III. 0·2368 gram substance gave 0·1145 OH_2, 0·3039 CO_2, and 0·1084 Ag.

	Found.			Theory for $\left\{\begin{matrix}C_6H_{13}\\COOAg\end{matrix}\right.$
	I.	II.	III.	
C	35·55	35·13	35·00 per cent.	35·44 per cent.
H	5·56	5·50	5·37 „	5·48 „
Ag ..	45·66	45·79	45·77 „	45·57 „

It was, therefore, heptoate of silver. The products of the oxidation of the aldehyde $C_{14}H_{28}O$, by means of chromic acid and acetic acid, are therefore carbonic anhydride, and heptoic and hexoic acids, according to the equation—

$$C_{14}H_{28}O + 3O_2 = \left\{\begin{matrix}C_5H_{11}\\COOH\end{matrix}\right. + \left\{\begin{matrix}C_6H_{13}\\COOH\end{matrix}\right. + CO_2 + OH_2.$$

Oxidation with silver oxide was next tried.

This experiment was made in the same way as with the aldehyde $C_{14}H_{26}O$, Part I. The acids obtained were carefully fractioned. By far the largest fraction obtained boiled between 195—230°; there was, however, a small quantity of a dark-brown residue left, which was reserved for distillation *in vacuo*. The distillate 195—230° was converted into a potassium and then into a barium compound. This dried at 120—130° gave on analysis the following results:—

I. 0·1666 gram substance gave 0·1013 $BaSO_4$ = 35·79 per cent. Ba.
II. 0·1290 „ „ 0·0785 „ = 35·78 „ „
Calculated for heptoate of barium ..... 34·70 per cent.
„ „ hexoate of barium ..... 37·33 „

This barium compound was therefore a mixture of barium hexoate and heptoate, the two acids being formed as in the case of the oxidation by means of chromic acid.

The dark-brown residue remaining in the retort above 230° was first distilled under a pressure of 300°, when most of it came over at about 230°. This was then carefully fractioned at the ordinary pressure. After a small quantity of heptoic acid had passed over, the thermometer rose rapidly to 300°, almost all the product (about $1\frac{1}{2}$ grams) distilling between 300—310°. On analysis it gave the following numbers:—

I. 0·0967 gram substance gave 0·1029 OH_2 and 0·2623 CO_2.
II. 0·1341 „ „ 0·1428 „ 0·3620 „

	Found. I.	Found. II.	Theory for $C_{14}H_{28}O_2$.
C	73·97	73·59 per cent.	73·60 per cent.
H	11·82	11·83 „	12·28 „

This acid, therefore, has the formula $C_{14}H_{28}O_2$. It is an almost colourless oil, which distils at the ordinary pressure, apparently without the least decomposition. The yield from the aldehyde $C_{14}H_{28}O$ is very small, so that it was found impossible to prepare salts pure enough for analysis.

This acid dissolves in ammonia, but the ammonium salt, on standing, quickly deposits an oil which may possibly be the amide of the acid.

The potash salt is a soap, and difficult to obtain pure. It is formed by shaking the acid with very dilute potash; on evaporating, however, it appears to decompose. The formation of this acid from the aldehyde may be expressed thus:—

$$C_{14}H_{28}O + O = C_{14}H_{28}O_2.$$

By cooling to $-10°$ it becomes very thick, but was not obtained in a solid condition.

As it seemed possible that the acid just described might be obtained in larger quantity from the aldehyde by employing an alkaline solution of potassium permanganate, the following experiment was made. About 20 grams of $C_{14}H_{28}O$ were mixed with rather more than the calculated quantity of permanganate dissolved in dilute soda, and from time to time the mixture was well shaken up. The oxidation took place rapidly at first, but afterwards proceeded very slowly. At the end of a week alcohol was added, and the soda solution separated from the precipitated hydrate of manganese by filtering through glass wool. The acids which had been formed were then liberated with hydrochloric acid, taken up with ether, and fractioned. However, almost all the acids came over between 200—230°, and only a trace of an acid with a high boiling point was present; this, however, appeared to boil at the same temperature as that obtained by the oxidation with silver oxide. The fraction boiling between 200—230° was converted into potash salts, purified as usual with absolute alcohol, and the silver salts precipitated with nitrate of silver. Analysis gave the following result:—

0·3208 gram substance gave 0·1475 OH_2, 0·3896 CO_2, and 0·1567 Ag.

	Found.	Theory for $C_5H_{11}COOAg$.	Theory for $C_6H_{13}COOAg$.
C	33·12 per cent.	32·28 per cent.	35·44 per cent.
H	5·11 „	4·93 „	5·48 „
Ag ..	48·84 „	48·43 „	45·57 „

It was therefore a mixture of hexoate and heptoate of silver. The products of the oxidation of $C_{14}H_{28}O$ are therefore carbonic anhydride, heptoic and hexoic acids, and $C_{13}H_{27}COOH$.

Several attempts were made to purify the neutral oils which were obtained in these experiments by fractional distillation, but although several anaylses were made of different fractions, no good results could be obtained. They begin to boil at 250°, but by far the greater part boil above 360°.

Action of Nascent Hydrogen on the Aldehyde $C_{14}H_{28}O$.

The crystalline body, $C_{14}H_{28}O$, being an aldehyde, it was thought interesting to try the action of nascent hydrogen on it, in order, if possible, to get the corresponding alcohol $C_{14}H_{30}O$. This would have the same formula as that previously obtained by the action of nascent hydrogen on the alcohol $C_{14}H_{28}O$ (Part I, p. 56). The experiment was made in the following way: The aldehyde was first dissolved in glacial acetic acid, and zinc turnings added, the whole being warmed on a water-bath. It was found advantageous to cover the surface of the zinc with copper, by dipping it in a solution of sulphate of copper, the action being thus very much accelerated. From time to time small quantities of water were added; the mixture was heated at last nearly to boiling. Water was then added in excess, and after nearly neutralising the acetic acid with potash, the oil was separated and well washed. On distilling, there still appeared to be a considerable quantity of unchanged aldehyde present, the product was, therefore, again treated with nascent hydrogen. This time, however, the oil was dissolved in ether and treated with water and sodium in exactly the same way as was employed in the reduction of œnanthaldehyde, as it was found to give better results than zinc and acetic acid. After a considerable excess of sodium had been added, the oil was extracted from the aqueous solution with ether, then dried and fractioned. After the ether had been distilled off, the principal quantity of the product came over between 260—290°, only a small residue remaining behind in the retort.

This distillate was then several times carefully fractioned, the largest part obtained boiling between 270—275°.

On analysis it gave the following numbers :—

0·1500 gram substance gave 0·1881 OH_2 and 0·4304 CO_2.

	Found.	Theory for $C_{14}H_{30}O$.
C	78·25 per cent.	78·50 per cent.
H	13·93 ,,	14·02 ,,

It therefore has the formula $C_{14}H_{30}O$.

It is a colourless oil, having but little odour. Cooled down to — 10° it solidifies to a waxy mass, which melts again at the ordinary temperature. It does not oxidise in contact with the air. When dissolved in carbon disulphide, and cooled down to — 10°, it does not take up bromine. It is soluble in most of the ordinary solvents. Its specific gravity is

at 15° = 0·8368
at 30 = 0·8301
at 35 = 0·8279

compared with water at the same temperatures. It is, without doubt, the same alcohol as that previously obtained by the action of nascent hydrogen on the unsaturated alcohol $C_{14}H_{28}O$, as it has the same boiling point. To further establish this, however, the acetate was prepared by heating it in a sealed tube with excess of acetic anhydride at 180° for two days. On the first distillation almost all the oily product distilled over between 270°—285°, very little residue being left in the retort.

On repeating the fractioning, the principal portion came over between 275—280°. On analysis it gave the following numbers:—

0·1165 gram substance gave 0·1310 OH_2 and 0·3210 CO_2.

	Found.	Theory for $C_{14}H_{29}OC_2H_3O$.
C	75·14 per cent.	75·00 per cent.
H	12·49 ,,	12·50 ,,

The numbers agree therefore with those required for the formula $C_{14}H_{29}O.C_2H_3O$.

In order to prove that this body is an acetate, a determination of the acetic acid, formed by its saponification, was made, which gave the following numbers:—

3·5293 grams substance gave 1·3065 grams potassium acetate = 22·67 per cent. $C_2H_4O_2$. The formula $C_{14}H_{29}O.C_2H_3O$ requires 23·43 per cent.

This acetate is a beautiful colourless oil, possessing an aromatic odour. It boils at the same temperature as that described in Part I (275—280°). It refracts light very strongly. Cooled to — 10° it does not solidify. When warmed with alcoholic potash it is very easily decomposed into potassic acetate and the alcohol $C_{14}H_{30}O$. Its specific gravity is

at 15° = 0·8559
at 30 = 0·8476
at 35 = 0·8448

compared with water at the same temperatures.

It is therefore seen that both the aldehyde $C_{13}H_{27}COH$, and the alcohol $C_{14}H_{27}OH$, when treated with nascent hydrogen, yield the same body, viz., the alcohol $C_{14}H_{29}OH$.

Theoretical Remarks.

As the aldehyde $C_{14}H_{28}O$ splits up on oxidation into heptoic, hexoic, and carbonic acids, according to the equation—

$$C_{14}H_{28}O + 3O_2 = \left\{\begin{matrix} C_5H_{11} \\ COOH \end{matrix}\right. + \left\{\begin{matrix} C_6H_{13} \\ COOH \end{matrix}\right. + CO_2 + OH_2,$$

it must have the following constitution:—

$$\begin{matrix} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2 \\ CH_3.CH_2.CH_2.CH_2.CH_2.CH.COH. \end{matrix}$$

This shows that it is a saturated body. It is isomeric with the alcohol $C_{14}H_{28}O$ described in Part I, obtained by the action of nascent hydrogen on the aldehyde $C_{14}H_{26}O$.

This aldehyde $C_{14}H_{28}O$ contains the group $\begin{matrix} —CH_2 \\ | \\ —CH.COH \end{matrix}$, whereas the alcohol contains the group $\begin{matrix} —CH \\ \| \\ —C.CH_2OH \end{matrix}$.

The production of this aldehyde is somewhat difficult to understand, as it is not formed by the action of nascent hydrogen on the aldehyde $C_{14}H_{26}O$. It would seem to be probably formed by the action of the nascent hydrogen at the moment of the condensation of the œnanthaldehyde. A further attempt to obtain it from the aldehyde $C_{14}H_{26}O$ was made by dissolving the latter in ether, cooling in a freezing mixture, and then adding bromine. As soon as this was no longer decolorised, water was added and then sodium, till a small quantity of the ethereal solution taken out was found no longer to contain bromine. The ether was then distilled off, and the residual oil fractioned.

A considerable quantity came over between 270—280°, which on combustion gave numbers agreeing fairly well with the formula $C_{14}H_{30}O$; it was therefore apparently the same alcohol as that obtained by the action of nascent hydrogen on the aldehyde and alcohol $C_{14}H_{28}O$. On heating with acetic anhydride in a sealed tube, it also gave an acetate. It is quite possible that some of the aldehyde $C_{14}H_{28}O$ was formed in this experiment, but could not be separated from the alcohol $C_{14}H_{30}O$. The aldehyde $C_{14}H_{28}O$ is isomeric with myristic aldehyde, which F. Krafft (*Ber.*, **13**, 1415) obtained by the dry distil-

lation of a mixture of barium myristate, barium formate, and lime. It melts at 52·5°, or 23° higher than my product.

The constitution of the acid $C_{14}H_{28}O_2$ obtained by the oxidation of the aldehyde $C_{14}H_{28}O$, is represented thus:—

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2$$
$$CH_3.CH_2.CH_2.CH_2.CH_2.\dot{C}H.COOH.$$

It is therefore heptylpentylacetic acid. It also appears to be formed by the action of alcoholic potash on the aldehyde $C_{14}H_{28}O$ in the same way as the corresponding acrylic acid $C_{14}H_{26}O_2$ is obtained from the aldehyde $C_{14}H_{26}O$. In the oxidation of the aldehyde $C_{14}H_{28}O$, it is probable that this acid is first formed, and then on account of its easy oxidisability is quickly converted into hexoic and heptoic acids. This acid is isomeric with myristic acid, which Krafft (*Ber.*, **12**, 1669) obtained by saponifying nutmeg oil. He describes it as a solid body melting at 53·8°, but gives no particulars as to its constitution.

The body having the formula $C_{21}H_{40}O$, which is formed by the union of 3 mols. of œnanthaldehyde, according to the following equation:—

$$3C_7H_{14}O + H_2 = C_{21}H_{40}O + 2H_2O,$$

has probably the following constitution:—

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2\ CH$$
$$\|$$
$$CH_3.CH_2.CH_2.CH_2.CH_2.C.CH_2$$
$$|$$
$$CH_3.CH_2.CH_2.CH_2.CH_2.CH.COH.$$

This is borne out by the fact that when dissolved in carbon disulphide and cooled down to −10°, it takes up 2 atoms of bromine, showing that it is unsaturated. The constitution of the alcohol $C_{14}H_{30}O$, obtained by the action of nascent hydrogen on the aldehyde $C_{14}H_{28}O$, and the alcohol isomeric with it, has already been referred to in Part I. It is isomeric with myristic alcohol, which is contained in spermaceti, together with cetyl alcohol and other bodies.

Polymerisation of Œnanthaldehyde.

Bruylants (*Ber.*, **8**, 415) has shown that by the action of dry potassium carbonate on œnanthaldehyde a solid polymeride of this body is produced, and it was thought that it would be of interest to make some experiments with this compound, with a view, if possible, of getting some clue as to its molecular weight, and also of comparing it with aldol. Borodin mentions that these two bodies appear to be closely related, both of them losing water on distillation, aldol giving

crotonic aldehyde; while the polymeride of œnanthaldehyde gives the bodies $C_{14}H_{26}O$ and $C_{28}H_{54}O_3$, œnanthaldehyde being also apparently regenerated. The latter reaction seems, however, to be more complicated than that with aldol, and the formation of the body $C_{28}H_{54}O_3$ would appear to indicate that the polymeride contained more than twice $C_7H_{14}O$. The polymeride was prepared as follows by the method used by Bruylants:—

100 grams of œnanthaldehyde were mixed with about 20 grams of dry potassium carbonate, and allowed to stand at ordinary temperatures, the formation of the polymeride generally requiring about four days. It is, however, hastened by gently warming and shaking the mixture from time to time at about 40—45°; the polymerisation is then generally complete in 5—6 hours, the aldehyde becoming quite solid. In order to ensure the polymerisation of all the œnanthaldehyde the mass was melted at 60°, shaken up with a small quantity of fresh potassium carbonate, and left to crystallise.

The product was carefully melted, and well washed with warm water, taking care that the temperature was not above 70°. As soon as all the carbonate was dissolved out the water was separated as much as possible, and the oil left to crystallise over sulphuric acid. This generally requires about two days. It was then placed in a vessel with a capillary tube at the bottom end connected with a vacuum pump. On working this, the oil was gradually drawn off, leaving the nearly pure polymeride as a white waxy crystalline mass In order to free it perfectly from oil, it was pressed between filter-paper, moistened with ether, and again pressed. Obtained in this manner, it melted at 52—53°, which corresponds with the melting point found by Bruylants. The oil which was drawn off from the crystals on standing for some time at 0°, deposits a further quantity of this body in crystals—generally as long needles. By repeating this cooling process, most of the product is eventually obtained in a solid state, only a very small quantity of oil remaining. The polymeride of œnanthaldehyde is very easily soluble in alcohol, ether, chloroform, carbon disulphide, petroleum, ether, &c., but it could not be crystallised from these solvents. It reduces an ammoniacal solution of oxide of silver very readily. If bromine be added to a solution of this body in carbon disulphide and cooled in a freezing mixture, it is not decolorised.

It was analysed, and gave the following numbers:—

0·2255 gram substance gave 0·2500 OH_2 and 0·6079 CO_2.

	Found.	Theory for $(C_7H_{14}O)_n$.
C	73·53 per cent.	73·68 per cent.
H	12·32 „	12·28 „

As already stated, it melts at 52—53°, and decomposes on heating above 115°. The decomposition seems to begin at that temperature, water being given off, and collecting at the top of the vessel in which it is heated, as a cloud. In order to examine the decomposition-products of this body, 50 grams were distilled in a stream of carbonic anhydride. The substance first melts, and at about 120° froths up a little. Between 120° and 200° a good deal came over, the thermometer then rose rapidly to 270°, and between this and 300° the amount which distilled over was considerable. A small residue remained behind, which was reserved for distillation in a vacuum. It was noticed that when the substance was quickly distilled, the residue was very small, whereas if the decomposition is allowed to take place slowly, the amount of residue is increased. The oil boiling between 120—200° was then several times carefully fractioned in a current of carbonic anhydride, nearly all of it at last coming over between 152—154°, and smelling strongly of œnanthaldehyde. Shaken up with a solution of hydrogen sodium sulphite it combined directly, and on analysis gave the following numbers:—

0·0929 gram substance gave 0·0988 OH_2 and 0·2507 CO_2.

	Found.	Calculated for $C_6H_{13}COH$.
C	73·59 per cent.	73·68 per cent.
H	11·81 „	12·28 „

It was therefore œnanthaldehyde. The fraction 270—290° was then several times fractioned in an atmosphere of carbonic anhydride. Almost all came over at last between 275—280°, and gave the following numbers on analysis:—

0·2414 gram substance gave 0·2700 OH_2 and 0·7063 CO_2.

	Found.	Calculated for $C_{14}H_{26}O$.
C	79·79 per cent.	80·00 per cent.
H	12·43 „	12·38 „

It was therefore the aldehyde $C_{14}H_{26}O$, and was undoubtedly identical with that obtained from œnanthaldehyde by the action of alcoholic potash, and described in Part I. Its specific gravity was practically the same, viz., 0·8504 at 15°, as compared with 0·8494. Dissolved in carbon disulphide it combines with bromine without evolution of hydrobromic acid, and does not solidify at −15°. It may be mentioned that by the decomposition of the polymeride of œnanthaldehyde by distillation, œnanthaldehyde and the body $C_{14}H_{26}O$ are easily obtained in a pure state, as the decomposition takes place nearly quantitatively, only a very small residue being formed. The two bodies are very easily separated by fractional distillation,

œnanthaldehyde boiling at 154°, and the aldehyde $C_{14}H_{26}O$ at 179°. The residues boiling above 290° (collected from a series of experiments) were first distilled in a vacuum, and then fractioned under a pressure of 250 mm. At the first distillation nearly all came over between 310—350° as a light yellow oil.

This fraction was then several times carefully fractioned under the same pressure, when most of it boiled at 330—340°, and gave the following numbers on analysis:—

I. 0·1211 gram substance gave 0·1349 OH_2 and 0·3427 CO_2.
II. 0·1324 „ „ 0·1474 „ 0·3737 „

	Found. I.	Found. II.	Theory for $C_{28}H_{54}O_3$.
C	77·18	76·98 per cent.	76·71 per cent.
H	12·37	12·37 „	12·33 „

This body seems therefore to have the composition $C_{28}H_{54}O_3$. It is an oil of a slightly yellow colour and disagreeable smell, which does not solidify when cooled down to $-10°$. When dissolved in carbon disulphide and cooled down to $-10°$, it takes up bromine without evolution of hydrobromic acid. Quantitative experiments were made with a view of determining the degree of unsaturation of the body, and gave numbers which agreed fairly well with those calculated for the formula $C_{28}H_{54}O_3Br_2$; but on titration with bromine, after a certain point is reached, the oil becomes slightly brown, and this makes it difficult to ascertain accurately when the bromine ceases to be taken up. It is apparently formed by removal of the elements of water from 4 mols. of œnanthaldehyde. Thus:—

$$4C_7H_{14}O = C_{28}H_{54}O_3 + OH_2.$$

This body reduces ammoniacal silver solution. On heating it with strong alcoholic potash it becomes brown, apparently being converted into higher condensation-products. A small quantity of potash compound was formed at the same time, which appeared to be potassium heptoate. Boiling with dilute sulphuric acid also decomposes this oil.

The polymeride of œnanthaldehyde splits up, therefore, on distillation into water, œnanthaldehyde, the aldehyde $C_{14}H_{26}O$, and the body $C_{28}H_{54}O_3$. These results therefore agree with those obtained by Borodin.

In order, if possible, to get some idea as to the molecular weight of this polymeric modification of œnanthaldehyde, it was thought that by carefully distilling known quantities and then weighing the decomposition-products, *i.e.*, the œnanthol $C_{14}H_{26}O$ and the residue, some

relation might be found which would point to a probable formula. The following results were obtained from three experiments made with the pure substance:—

I. 8·9 grams polymeride gave on distillation 4·5 grams crude œnanthaldehyde and water, 3·7 grams $C_{14}H_{26}O$, and 0·6 gram residue (= $C_{28}H_{54}O_3$).

II. 33·3 grams polymeride gave 16·3 grams œnanthaldehyde and water, 14·1 grams $C_{14}H_{26}O$, and 1·3 gram residue boiling above 285°.

III. 33·2 grams polymeride gave 16·7 grams œnanthaldehyde and water, 14·3 grams $C_{14}H_{26}O$, and 0·9 gram residue.

The residue was all that boiled above 285°, and possibly still contained small quantities of $C_{14}H_{26}O$. These three experiments were purposely made from three different preparations. The last one was made from crystals which had separated out from the oil (obtained by filtering the crude polymeride), on standing for some weeks at 0°. The water can be calculated on the supposition that for every molecule of $C_{14}H_{26}O$ that is formed, one molecule of water is separated, which then gives the following results for œnanthaldehyde and water:—

I. Water calculated = 0·3 gram, therefore œnanthaldehyde = 4·2 grams.

II. Water calculated = 1·2 gram, therefore œnanthaldehyde = 15·1 grams.

III. Water calculated = 1·2 gram, therefore œnanthaldehyde = 15·5 grams.

Calculated into percentages, the polymeride gives on distillation:—

	I.	II.	III.
Œnanthaldehyde	47·19	45·34	46·68
$C_{14}H_{26}O$	41·58	42·34	43·07
Water.....	3·37	3·60	3·61
Residue	6·74	3·93	2·71

These numbers show that equal weights of œnanthaldehyde and $C_{14}H_{26}O$ (+ water) are formed by the destructive distillation of the polymeride, *i.e.*, two molecules of œnanthaldehyde and one of $C_{14}H_{26}O$, probably according to the equation:—

$$(C_7H_{14}O)_4 = 2C_7H_{14}O + C_{14}H_{26}O + OH_2.$$

It appears therefore likely that the polymeride is formed from four molecules of œnanthaldehyde, and has the following constitution:—

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH(OH)$$
$$CH_3.CH_2.CH_2.CH_2.CH_2.CH.CH(OH)$$
$$CH_3.CH_2.CH_2.CH_2.CH_2.CH.CH(OH)$$
$$CH_3.CH_2.CH_2.CH_2.CH_2.CH.COH.$$

That it is a saturated body is proved by the fact, that this substance when dissolved in bisulphide of carbon, does not take up bromine without evolution of hydrobromic acid, and, if it is an aldehyde, this must also be the case from its formula. The different groups in this formula are linked together much in the same way as those in aldol, which splits up into water and crotonic aldehyde according to the equation:—

$$\begin{array}{l} CH_3 \\ CH(OH) \\ | \quad | \\ CH \quad H \\ COH \end{array} = \begin{array}{l} CH_3 \\ CH \\ \| \\ CH \\ COH \end{array} + OH_2$$

It is also very easy to understand the splitting up of the polymeride of œnanthaldehyde, in a similar way, into water, the aldehyde $C_{14}H_{26}O$, and two molecules of œnanthaldehyde; thus:—

$$\begin{array}{l} CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ CHO- \end{array} \quad \begin{array}{l} \\ CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ H.CH \end{array} \quad \begin{array}{l} \\ \\ CHO- \end{array} \quad \begin{array}{l} \\ \\ CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ H.CH \end{array} \quad \begin{array}{l} \\ \\ \\ CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH(OH) \end{array} \quad \begin{array}{l} \\ \\ \\ \\ \\ \\ -CH \\ COH \end{array}$$

$$= \begin{array}{l} CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ COH \end{array} + \begin{array}{l} \\ CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ COH \end{array} + \begin{array}{l} \\ \\ CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH=C \end{array} \quad \begin{array}{l} \\ \\ \\ CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ COH \end{array}$$

$$+ HOH$$

The amount of the body $C_{28}H_{54}O_3$ formed is dependent, as before mentioned, on the rapidity of the distillation. In Experiment I, for example, the polymeride was slowly distilled, and 6·74 per cent. of residue was obtained; whereas in Experiment III the retort was heated with an open flame and the distillation conducted very rapidly when only 2·71 per cent. of residue was obtained. The amount obtained has rarely reached more than 10 per cent. The formation of this substance from the polymeride of œnanthaldehyde is in itself in

favour of this latter substance being built up from four molecules of œnanthaldehyde, as the formation of the former is then very easy of explanation; thus:—

$$C_{28}H_{56}O_4 = C_{28}H_{54}O_3 + OH_2.$$

It would be difficult to understand how such a body could be produced by the simple distillation of a mixture of œnanthaldehyde and the aldehyde $C_{14}H_{26}O$. Its constitution may probably be represented thus:—

$$\begin{array}{l} CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH(OH) \\ \quad CH_3.CH_2.CH_2.CH_2.CH_2.\dot{C}H.CH(OH) \\ \qquad CH_3.CH_2.CH_2.CH_2.CH_2.\dot{C}H.CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \| \\ \qquad\quad CH_3.CH_2.CH_2.CH_2.CH_2.C.COH. \end{array}$$

This shows it to be an unsaturated body, which is borne out by its combining directly with bromine. By the action of solid potash at ordinary temperatures on œnanthaldehyde, Borodin states that he obtained two different polymerides; the one solid and the other liquid. In order to see if this were the case when potassium carbonate was used, the oil which was filtered off from the solid polymerides was allowed to stand at 0° till it deposited no more crystals, and then completely filtered off. Only a small quantity of oil was obtained, having the appearance of glycerol, and smelling strongly of œnanthaldehyde, whereas the solid product has very little smell. It was then left for some time over sulphuric acid. On heating, the oil began to decompose at 120°, giving off water; at a temperature of 130—140° the decomposition was very rapid. In order to see whether it were a different polymeride or only the solid one mixed with a little impurity which prevented its crystallising, two quantitative experiments were made and the distillation-products weighed as before. They gave the following results:—

I. 21·6 grams of the oil gave 10·3 grams crude œnanthaldehyde and water, 8·1 grams $C_{14}H_{26}O$, and 2·4 grams residue.

II. 12·2 grams gave 5·7 grams œnanthaldehyde and water, 4·6 grams $C_{14}H_{26}O$, and 1·0 gram residue.

If the water be calculated as before, the following amounts of œnanthaldehyde and water are obtained:—

I.	Water calculated	= 0·7 gram.	Œnanthaldehyde	= 9·6 grams.
II.	„	= 0·4 gram.	„	= 5·3 „

Calculated into percentages these give the following numbers, as the relative amounts of œnanthaldehyde and $C_{14}H_{26}O$ formed:—

Œnanthaldehyde	44·44	43·47 per cent.
Water	3·24	3·28 ,,
$C_{14}H_{26}O$	37·50	37·70 ,,
Residue	11·11	8·19 ,,

These two experiments were made from two different preparations. From these results, it appears that the oil is most probably only a mixture of the solid polymeride and a little unchanged œnanthaldehyde. By the action of potassium carbonate on œnanthaldehyde, it seems therefore that only one polymeride is formed, which is solid and melts at 52—53°. By boiling œnanthaldehyde with potassium carbonate, the same condensation-products are produced as by the distillation of the polymeride, together with potassium heptoate. It is probable that the polymeric modification of isobutaldehyde, which Urech (*Ber.*, **12**, 190; **13**, 483 and 590) obtained by the action of potassium carbonate on that aldehyde at ordinary temperatures, is derived from at least four molecules of isobutaldehyde. Urech considers that it has the constitution $(C_4H_8O)_3$, and describes it as a very thick oil, which can be distilled in steam. When distilled, alone, however, it decomposes into water, isobutaldehyde and condensation-products. From these he isolated a body, $C_{12}H_{22}O_2 = 3C_4H_8O - OH_2$.

Demtschenko (*Ber.*, **6**, 1176) also obtained a polymeride by the action of sulphuric acid on isobutaldehyde, which has the formula $(C_4H_8O)_3$, and which he called "paraisobutaldehyde." It distils without decomposition, and he was thus able to determine its molecular weight by taking its vapour-density; this agreed with the formula $(C_4H_8O)_3$. It therefore appears that the polymeride obtained by Urech is quite a different body, possibly containing at least $4(C_4H_8O)$.

The same remark applies to the polymeride obtained by Borodin (*Ber.*, **6**, 982) from isovaleraldehyde, which, on distillation, splits up into water, isovaleraldehyde, $C_{10}H_{18}O$, and $C_{20}H_{38}O_2$, and the hydrate of which is produced by the action of soda solutions on this aldehyde at ordinary temperatures. This latter body has the formula $(C_{10}H_{20}O_2)_2H_2O = (C_5H_{10}O)_4H_2O$.

By distillation, this hydrate also splits up into water, isovaleraldehyde, $C_{10}H_{18}O$, and $C_{20}H_{38}O_2$.

Action of Nascent Hydrogen on Polymerised Œnanthaldehyde.

This experiment was made in the hope of obtaining from the polymerised œnanthaldehyde, a glycol of the formula $C_{28}H_{58}O_4$, by the reduction of the COH-group to CH_2OH, and of thus confirming the supposition that it is derived from 4 mols. of œnanthaldehyde.

Thirty grams of the polymeride were dissolved in ether, and then treated with 50 per cent. acetic acid, and a large excess of sodium in a flask connected with a reversed condenser. The sodium was added very slowly, and now and then a little acetic acid was poured in, to insure the contents having an acid reaction, as it appeared probable that the polymeride would be easily decomposed by caustic alkali. At the end of the reaction the ethereal solution was well washed to remove sodium acetate and acetic acid, dried, and the ether distilled off. The residual oil was then carefully fractioned. The first fraction obtained was from 100—210°, and weighed about 5 grams; the thermometer then rose rapidly to 260°, and between this and 300° about 5 grams more came over. The greater part, however, boiled above 310°, and was left behind in the retort. The product which came over between 100—210° was then repeatedly fractioned, when at last most of it came over between 174—176°, and gave the following numbers on analysis:—

0·1535 gram substance gave 0·1857 OH_2 and 0·4121 CO_2.

	Found.	Calculated $C_6H_{13}CH_2OH$.
C	73·22 per cent.	72·41 per cent.
H	13·44 „	13·79 „

It is therefore undoubtedly heptyl alcohol. On shaking it with acid sodium sulphite, a small quantity of a compound was formed, indicating that a trace of œnanthaldehyde was also present. This would account for the hydrogen being low and the carbon high in the above analysis.

The oil boiling between 250—310° was then repeatedly fractioned; a product was thus obtained boiling at 297—300°. The quantity was, however, very small, so that it was very difficult to obtain pure. It gave on analysis the following numbers:—

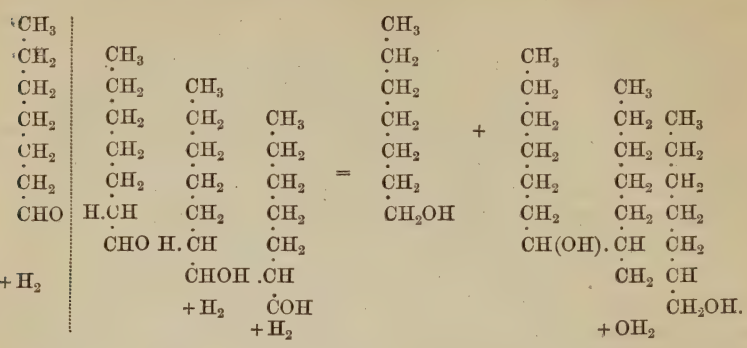
I. 0·2563 gram substance gave 0·3133 OH_2 and 0·7268 CO_2.
II. 0·1746 „ „ 0·2133 „ 0·4936 „

	Found.		
	I.	II.	Theory $C_{21}H_{44}O_2$.
C.....	77·34	77·10 per cent.	76·83 per cent.
H	13·58	13·57 „	13·41 „

This substance therefore appears to have the formula $C_{21}H_{44}O_2$. Its formation, together with that of heptyl alcohol by the action of nascent hydrogen on the polymeride of œnanthaldehyde, may be represented thus:—

$$C_{28}H_{56}O_4 + 3H_2 = \left\{ \begin{matrix} C_6H_{13} \\ CH_2OH \end{matrix} \right. + C_{21}H_{44}O_2.$$

This reaction can be better understood if the equation is written out as follows; thus:—



This substance is a yellowish oil, which does not solidify at — 20°. If dissolved in carbon disulphide and cooled down to — 10°, it does not appear to take up bromine. In order to confirm its molecular weight several attempts were made to determine its vapour-density, but as it decomposes a few degrees above its boiling point, no useful results were obtained.

I hope to have another opportunity of more thoroughly studying this interesting reaction, and more especially of examining the products boiling above 310°, which, as yet, I have not been able to obtain pure.

Action of Alcoholic Potash on Acetic Aldehyde.

A few experiments were made on the action of very dilute alcoholic potash on ordinary aldehyde, in order to see if it were possible to obtain as good a yield of crotonic aldehyde by this reaction, as of the corresponding aldehyde, $C_{14}H_{26}O$, from œnanthaldehyde, more especially as the preparation of the former by the zinc chloride reaction is unsatisfactory, the yield being very small.

The aldehyde employed in these experiments was the so-called "concentrated solution" from Kahlbaum, which is a mixture of water, aldehyde, and a trace of alcohol. The aldehyde was mixed with a little alcohol, and then treated every day with small quantities of alcoholic potash, cooling the mixture well after each addition. After standing for some time, a considerable quantity of metaldehyde separated out in large crystals, which were filtered off. From the solution an oil was obtained, which, after washing with a solution of calcium chloride and drying, was fractioned. At first a considerable quantity of unchanged aldehyde came over, then from 90—135°

a large fraction was obtained; above 130° a dark brown residue was left, which probably contained aldol, as on further heating it decomposed, giving off water and a small quantity of an oil smelling very like crotonic aldehyde.

The product boiling between 90—135° was carefully fractioned in carbonic anhydride. Two fractions were obtained between 100—110° and 115—130°. The latter was by far the larger. On repeatedly fractioning the first of these, nearly all of it boiled between 102—106°, and gave the following numbers on analysis:—

0·2093 gram substance gave 0·1636 OH_2 and 0·5229 CO_2.

	Found.	Calculated $CH_3.CH=CH.COH$.
C.....	68·14 per cent.	68·57 per cent.
H.....	8·68 „	8·57 „

It was therefore crotonic aldehyde. On standing for some few days in the air, it deposited crystals of crotonic acid, melting at 70°, whereas the pure acid melts at 72°. The second fraction, on being redistilled, eventually boiled mostly between 123—125°, and gave the following result on analysis:—

0·1264 gram substance gave 0·1014 OH_2 and 0·2509 CO_2.

	Found.	Calculated $(CH_3COH)_3$.
C	54·13 per cent.	54·54 per cent.
H.....	8·91 „	9·09 „

It was therefore paraldehyde. The yield of crotonic aldehyde was unfortunately small, but it appears probable that, by modifying the conditions, it might be improved, and this process found to be the easiest method of preparing it. Paraldehyde was the chief product of the reaction.

Finally, I append a table of the substances obtained from œnanthaldehyde, with their boiling points and specific gravities.

Name of substance.	Boiling point.	Specific gravity compared with water at the same temperature.		
		15°	30°	35°.
Œnanthaldehyde	153—154°	0·8231	0·8128	0·8099
$C_{14}H_{26}O = \left\{\begin{matrix} C_{13}H_{25} \\ COH \end{matrix}\right\}$..	277—279°	0·8494	0·8416	0·8392
$C_{13}H_{27}COH$	266—268° (m.p.—29·5°)	—	0·8274	0·8258
$C_{13}H_{25}CH_2OH$	280—283°	0·8520	0·8444	0·8418
$C_{13}H_{27}CH_2OH$	270—275°	0·8368	0·8301	0·8279
$C_{13}H_{25}CH_2OC_2H_3O$	285—290°	0·8680	0·8597	0·8568
$C_{13}H_{27}CH_2OC_2H_3O$	275—280°	0·8559	0·8476	0·8448
$C_{13}H_{25}COOH$	275—285° (at 250 mm.)	—	—	—
$C_{13}H_{27}COOH$	300—310°	—	—	—
$C_{21}H_{40}O$	310—315° (at 300 mm.)	0·8744	0·8665	0·8637
$C_{28}H_{50}O$	330—340° (at 200 mm.)	0·8831	0·8751	0·8723
$C_{28}H_{54}O_3$	330—340° (at 200 mm.)	—	—	—
$C_{28}H_{56}O_4$	melts at 52—53°	—	—	—
$C_{21}H_{44}O_2$	297—300°	—	—	—

I cannot conclude this paper without expressing my sincere thanks to Prof. Wislicenus, in whose laboratory this research was carried out, for his kind help and advice during its progress.

X.—*On the Condensation-products of Isobutaldehyde obtained by Means of Alcoholic Potash.*

By W. H. Perkin, Jun., Ph.D.

Condensation-products of Isobutaldehyde.

A short time ago there appeared in the *Berichte* (**15**, 2363) an abstract of a preliminary notice by Fossek (*Monatsh. f. Chem.* **3**, 622; *C. J.*, Abstr., 1882, 1274), on the action of an aqueous solution of caustic potash on isobutaldehyde. As I have for some time been working on the condensation-products of isobutaldehyde produced by means of alcoholic potash, in continuation of a research on the condensation of œnanthaldehyde, on which I have been engaged for the last two years, I am compelled to publish my results, although not quite completed,

especially as they are quite different from those obtained by Fossek, alcoholic potash seeming to bring about a series of reactions differing from those obtained by the action of aqueous potash. The method employed for preparing the isobutaldehyde was the following:—100 grams isobutylalcohol and 200 grams water were put into a large flask connected with a condenser, warmed up to about 50°, and a concentrated solution of bichromate of potash, mixed with an equal volume of sulphuric acid slowly run in, the contents of the flask being well shaken after each addition, to facilitate the escape of the aldehyde as soon as formed. This concentrated bichromate solution was added, until the oily layer of isobutyl alcohol disappeared from the surface of the mixture in the flask, and the whole was then boiled to drive off any aldehyde still remaining in the liquid.

The oily part of the distillate was separated from water, dried as quickly as possible with calcium chloride, and fractioned. The portion which distilled over below 100° was collected apart, and carefully fractioned by using a tube 3 feet high, to facilitate the separation of the aldehyde from the other products. By this means the aldehyde is easily obtained pure, boiling from 60—62°. The quantity was from 50—60 per cent. of the theoretical.

The condensation with alcoholic potash was first tried in the following way:—50 grams of isobutaldehyde were dissolved in 100 grams absolute alcohol, and then a solution of 2 grams potash in 20 grams alcohol slowly added, the temperature not being allowed to rise above 30°. The mixture after cooling was then mixed with a second 2 grams potash in alcohol, and after standing for 12 hours, warmed up to 50° for about 10 minutes. It is important not to warm too long, as otherwise the condensation is apt to go too far, and only high boiling condensation-products to be produced. The liquid was left to cool, and the saline products separated from the condensed oils, by adding much water and taking the oil up with ether. If the alcohol be first distilled off, the excess of potassium hydrate and saline matter act further on the aldehyde producing higher condensation-products. The aqueous saline solution from several experiments was first examined; it was thoroughly freed from oily products with ether, concentrated, and acidulated with hydrochloric acid. This caused the separation of some acids, which were extracted with ether. The ethereal solution was washed, dried over chloride of calcium, and distilled.

After the ether had distilled off, the principal part of the product came over between 145—180°. A considerable quantity afterwards passed over between 180° and 260°, leaving a thick tarry residue in the retort; the portion boiling at 145—180° consisted essentially of isobutyric acid. It was, however, purified, and converted into its silver salt. A silver determination gave the following numbers:—

0·3846 gram substance gave 0·2142 gram Ag = 55·69 per cent.
Calculated for $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.COOAg$ = 55·38 „

The fraction boiling between 180—260° was then several times carefully fractioned, when the largest part obtained boiled at 245—255°. This gave on analysis the following numbers:—

I. 0·1565 gram substance gave 0·1479 gram OH_2 and 0·3839 gram CO_2.

II. 0·1676 gram substance gave 0·1575 gram OH_2 and 0·4111 gram CO_2.

	Found. I.	Found. II.	Theory $C_{12}H_{22}O_3$.
C.....	66·90	66·89 per cent.	67·29 per cent.
H	10·50	10·44 „	10·28 „

These numbers therefore agree with those required by the formula $C_{12}H_{22}O_3$. The body is therefore an isomeride of octylacetoacetic acid; this acid is probably formed by the action of potash on the aldehyde $C_{12}H_{22}O_2$ (which will be found described further on) according to the equation—

$$2C_{12}H_{22}O_2 + KOH = C_{12}H_{21}O_3K + C_{12}H_{24}O_2.$$

This acid dissolves somewhat readily in dilute potash, but after standing for some time the potassium salt separates out as a gummy layer on the surface of the liquid. Attempts were also made to prepare the potassium salt by dissolving the acid in dilute alcoholic potash, passing CO_2, and filtering off the precipitated potassium carbonate, but in this case the potassium salt was left behind, on evaporating off the alcohol, as an uninviting soap. The acid itself is a light brown oil, having but little odour; it dissolves in ammonia, and precipitates silver from a solution of silver oxide in ammonia. It distils apparently without decomposition, cooled to −10°. It does not solidify.

By the action of aqueous potash on isobutaldehyde, Fossek obtains an acid to which he assigns the formula $C_8H_{16}O_3$; this requires $\begin{cases}C = 60·00 \text{ per cent.}\\H = 10·00 \text{ per cent.}\end{cases}$ It melts at 75—80°, and is therefore evidently quite different from the one described above.

The ethereal solution of the condensed oils was well washed. It was dried with chloride of calcium, and fractioned in a stream of carbonic anhydride. The fraction below 100° contained besides ether a considerable quantity of the unchanged aldehyde. That from 100—140° was very small, but between 140—180° a considerable quantity of a colourless oil was obtained, smelling strongly of camphor. The residue

in the retort was very small. The oil boiling between 140—180° was fractioned as rapidly as possible, when nearly the whole came over between 70—100°, and only a small quantity distilled over between 145—160°. There was also a considerable quantity of a high boiling product, which had been produced during the distillation, left behind.

This last fraction was once more rapidly fractioned, when the principal part distilled between 154—157°. On analysis it gave the following numbers:—

I. 0·1156 gram substance gave 0·1170 gram OH_2 and 0·3070 gram CO_2.

II. 0·1195 gram substance gave 0·1198 gram OH_2 and 0·3168 gram CO_2.

	Found.		
	I.	II.	Theory $C_{12}H_{22}O_2$.
C.....	72·52	72·30 per cent.	72·73 per cent.
H	11·24	11·14 „	11·11 „

This body appears to have the formula $C_{12}H_{22}O_2$, and is probably formed by the separation of a molecule of water from three molecules of isobutaldehyde, thus:—

$$3C_4H_3O = C_{12}H_{22}O_2 + H_2O.$$

It is a colourless oil, having a powerful ethereal smell and burning taste. It reduces an ammoniacal silver solution readily, and combines slowly with acid sulphite of sodium, forming an amorphous-looking mass, very slightly soluble in water, which under the microscope is seen to consist of small crystals displaying colours in polarised light. On the addition of an acid or of sodium carbonate this compound is decomposed, an oil separating out. It does not solidify when cooled down to −10°. If dissolved in carbon disulphide, and the solution cooled in a freezing mixture, it takes up bromine. It is easily decomposed by potash, apparently forming a considerable quantity of potassium isobutyrate. This oil is probably the same body as that which Urech obtained (*Ber.*, **13**, 590) by distilling the polymerised modification of isobutaldehyde produced by the action of potassium carbonate. He describes it as a colourless oil, possessing an ethereal smell, and boiling at 154°. He also notices that on distilling it decomposes, leaving a high-boiling residue in the retort.

A vapour-density which he made agreed fairly well with the formula $C_8H_{14}O$, but on analysis numbers were obtained which agreed with the formula $C_{12}H_{22}O_2$. As the substance decomposes on prolonged heating, a vapour-density has probably but little value. Fossek, by the action of sodium acetate on aqueous potash, obtained an

aldehyde $C_8H_{14}O$, boiling at 149—151°, which, however, seems to be different from the one described above, as it appears to distil without decomposition. It requires 76·19 per cent. of carbon, whereas the substance examined by me contained 72·5. By the action of $ZnCl_2$ or PCl_3 on isobutaldehyde, Fossek obtains polymerides derived from 3 mols. of isobutaldehyde.

Action of Nascent Hydrogen on the Aldehyde $C_{12}H_{22}O_2$.

This experiment was tried in order, if possible, to obtain an alcohol from the aldehyde $C_{12}H_{22}O_2$, and by this means to obtain some further clue as to its constitution. About 50 grams of the aldehyde were dissolved in 200 grams of ether, mixed with a small quantity of water, placed in a large flask connected with a reversed condenser, and sodium was added at intervals and in small pieces, the mixture being kept as cool as possible, and shaken up from time to time to dissolve out any sodic hydrate suspended in the ether. The ethereal solution was then washed, dried, and fractioned. After the ether had distilled off, most of the oil came over between 260—280°, leaving however a small residue in the retort. This oil was slowly fractioned in a Wurtz flask, with a neck about 8 inches long, when the principal portion came over between 270—275° as a colourless oil, possessing a very strong odour. On analysis it gave the following numbers:—

I. 0·1038 gram substance gave 0·1219 gram OH_2 and 0·2721 gram CO_2.

II. 0·1160 gram substance gave 0·1341 gram OH_2 and 0·3029 gram CO_2.

	Found.		
	I.	II.	Theory $C_{12}H_{26}O_2$.
C.....	71·49	71·21 per cent.	71·28 per cent.
H	13·05	12·85 „	12·87 „

It appears therefore that an alcohol of the formula $C_{12}H_{26}O_2$, which is isomeric with ethyl propyl pinacone, had been formed, according to the equation—

$$C_{13}H_{22}O_2 + 2H_2 = C_{12}H_{26}O_2.$$

This body does not solidify at −10°, neither does it combine with acid sodium sulphite. On distillation it appears to decompose slightly, forming lower and higher fractions. This makes it difficult to obtain it in the pure state. In order, if possible, to obtain an acetate from this body, it was treated with an excess of acetic anhydride at 180° for four hours, and then fractioned. After the anhydride and acetic acid had

been slowly distilled off, nearly all the residue boiled between 175—190°. This, on carefully refractioning, gave quantities of distillate of about the same size, boiling at 180—185° and 185—190°. Analysis of these gave the following numbers:—

I. (180—185°) 0·1298 gram substance gave 0·1245 gram OH_2 and 0·3211 gram CO_2.

II. (185—190°) 0·1336 gram substance gave 0·1311 gram OH_2 and 0·3305 gram CO_2.

	Found. I.	Found. II.	Theory. $C_{16}H_{30}O_4 = C_{12}H_{24}O_2(C_2H_3O)_2$.
C.....	67·46	67·46 per cent.	67·13 per cent.
H	10·66	10·90 „	10·48 „

These numbers indicate that both specimens consisted of a diacetate of the formula $C_{16}H_{30}O_4$. This substance would be produced according to the equation:—

$$C_{12}H_{26}O_2 + \left(\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>\!O\right)_2 = C_{12}H_{24}O_2(C_2H_3O)_2 + 2CH_3COOH.$$

A Dumas vapour-density determination was made of this body, and gave 6·289. The molecular weight should therefore be $6{\cdot}289 \times 28{\cdot}92 = 181{\cdot}87$, whereas the theoretical molecular weight for $C_{24}H_{42}O_6 = 286$, so that apparently in this case, as with the body $C_{12}H_{22}O_2$, decomposition takes place on prolonged heating of the vapour. This acetate is a very strong-smelling body, reminding one of peppermint. These results must only be looked upon as preliminary, as owing to the very small quantity of the aldehyde $C_{12}H_{22}O_2$, at my command, it has been, up to the present, impossible to confirm them.

In order to study the higher condensation-products the isobutaldehyde was treated in the same manner as in the previous experiment, twice as much potash, however, being employed, and the temperature of the reactions allowed to rise to 45°. At the conclusion of the operation the mixture was heated on the water-bath to near its boiling point for ten minutes; it was then diluted with water, and the neutral oils were taken up with ether, separated, and treated as before. On distillation a small quantity of oil came over under 200°, which contained, besides the aldehyde $C_{12}H_{22}O_2$, a small quantity of a body boiling between 190—200°; this gave on analysis, numbers approximately agreeing with the formula $C_{16}H_{30}O_3$; the quantity was, however, too small to further examine. After this the thermometer rose rapidly to 215°, and between this and 235° about 20 grams of oil distilled over, leaving in the retort a residue which was reserved for further examination (see p. 99).

On repeatedly distilling this oil in an atmosphere of carbonic anhydride, in a long-necked Wurtz flask, eventually two principal fractions were obtained, boiling between 223—224° and 224—225°; these gave on analysis the following numbers :—

I. 0·1307 gram substance gave 0·1363 gram OH_2 and 0·3381 CO_2.
II. 0·1778 „ „ 0·1833 „ „ 0·4576 „

	Found. I.	Found. II.		Theory for $C_{20}H_{38}O_4$.
C	70·55	70·19	per cent.	70·17 per cent.
H	11·58	11·45	„	11·11 „

This body appears therefore to have the formula $C_{20}H_{38}O_4$. Its formation is easily understood, thus :—

$$5C_4H_8O = C_{20}H_{38}O_4 + H_2O.$$

It is an almost colourless oil, which smells strongly of camphor. When it was left in contact with hydrogen sodium sulphite for two or three weeks, with constant agitation, long transparent needles were formed; it is therefore apparently an aldehyde. It does not solidify in a freezing mixture, but becomes extremely viscid. It reduces ammoniacal silver solution, but does not quickly absorb oxygen from the air. When heated for some hours with 50 per cent. sulphuric acid, it first becomes black, giving off a considerable quantity of CO_2, and at last it becomes nearly solid. Ether removes an oil from this product which principally distils between 200—240°. There was, however, also a low-boiling body present, which I hope to investigate further.

This aldehyde, $C_{20}H_{38}O_4$, is perhaps the same body as that which Urech obtained (*Ber.*, **13**, 593) by distillation of the polymeride of isobutaldehyde produced by the action of potassium carbonate. His product was an intensely yellow oil, boiling between 230—240°, and gave, on analysis, C = 71·50 per cent., H = 11·80 per cent.; considering the wideness of the range of boiling point, these agree fairly with the numbers which I obtained. He also determined the vapour-density by Hofmann's method, and found it equal to 6·80, which gives a molecular weight = 196·70 as against 342, calculated for $C_{20}H_{38}O_4$, so that it appears that this body decomposes on the prolonged heating of its vapour. In order to confirm these results, two vapour-density determinations were made, the first by the Dumas method, the second by the Victor Meyer method.

The vapour-density obtained by the Dumas method was 6·64, which agrees fairly with the one found by Urech. The one made by the Victor Meyer method gave 5·77.

The molecular weight was therefore 28·92 × 5·77 = 167.

This vapour-density was taken in a lead-bath, so that the body was probably fully decomposed, as this result is about half of the calculated density. It is worth noticing that during the determination by means of the Dumas method, most of the substance distilled off when the bath was up to 240°; but it was not till the bath had gone up to 252° that all was vaporised. This seems to be a clear indication of its decomposing, as the substance used boiled between 223—224°.

By the action of aqueous potash on isobutaldehyde, Fossek obtained a body boiling at 222—223°, and fusing at 15·5°, to which he gave the formula $C_8H_{18}O_2$. This formula requires C = 65·75 per cent., H = 12·33 per cent., and a molecular weight = 146. There is no doubt it is a different body from the one described above.

Action of Acetic Anhydride on $C_{20}H_{38}O_4$.

As it seemed possible that the aldehyde $C_{20}H_{38}O_4$ might, by the action of acetic anhydride, form some acetyl compound which would throw light on its constitution, the following experiments were made:—A quantity of this substance was first sealed up in a tube with a slight excess of acetic anhydride (for a monoacetate), and slowly heated till the temperature reached 180°, and then allowed to cool down. On fractioning the product as soon as the acetic anhydride and acetic acid had distilled off, nearly all came over between 235—250°. This was several times carefully fractioned, when at last the largest quantity was obtained boiling at 240—242°. On analysis it gave the following results:—

I. 0·1345 gram substance gave 0·1263 gram OH_2 and 0·3375 CO_2.
II. 0·1549 „ „ 0·1452 „ „ 0·3905 „

	Found. I.	Found. II.	Theory for $C_{22}H_{40}O_5$.
C	68·43	68·75 per cent.	68·75 per cent.
H	10·43	10·42 „	10·42 „

These numbers agree with those required for a monoacetate, produced according to the following equation:—

$$C_{20}H_{38}O_4 + \begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>\!O = C_{22}H_{40}O_5 + CH_3COOH.$$

This body is an almost colourless oil, having only a very faint smell. It does not solidify in a freezing mixture. Treated with potash it turns black, appearing to saponify very easily. In order to see if acetic anhydride had any further action on this body, it was heated in a sealed tube with excess of acetic anhydride to 200—220° for five

hours, and then refractioned. Nearly all of the oil came over between 240° and 255°. This when refractioned two or three times gave, as the principal part, an oil boiling constantly from 248—252°, and yielding on analysis the following numbers :—

I. 0·1344 gram substance gave 0·1189 OH_2 and 0·3217 CO_2.
II. 0·1372 „ „ 0·1235 „ 0·3389 „

	Found. I.	Found. II.		Theory for $C_{24}H_{42}O_6$.
C	67·31	67·37	per cent.	67·60 per cent.
H	9·83	10·00	„	9·86 „

This body may therefore be regarded as a diacetate derived from $C_{20}H_{38}O_4$, and produced from the monoacetate, according to the equation :—

$$C_{22}H_{40}O_5 + \begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>\!O = C_{24}H_{42}O_6 + CH_3COOH.$$

This diacetate resembles the monoacetate in most respects ; it is an almost colourless oil, has very little smell, and does not solidify in a freezing mixture. It distils without the least decomposition. In order to prove that this was really a diacetate, it was quantitatively saponified, and the acetic acid formed was determined. As there was not sufficient of the fraction 248—252°, a fraction boiling at 246—254° was taken, and gave the following results :—

4·1428 gram substance was saponified with alcoholic potash, water added, and the oil extracted with ether. The potash-solution was concentrated, acidulated with sulphuric acid, and distilled into baryta-water, and afterwards the excess of baryta was separated with carbonic anhydride. The weight of barium salt obtained, after evaporation, was 3·1862 grams. As the salt did not look pure, it was thought that it probably contained a small quantity of barium isobutyrate. A barium determination was therefore made which gave 52·74 per cent.

Theory for $Ba(C_2H_3O_2)_2 = 53·72$. This therefore apparently consisted of—

Barium acetate ..... 89·86 per cent. = 2·863 grams.
Barium isobutyrate.... 10·14 „ = 0·3231 gram.

Theory requires that from 4·1428 grams of the diacetate, 2·4800 grams of barium acetate should be formed, which agrees as well as could be expected with the quantity found. There is, therefore, no doubt that it was a diacetate. The dark-brown ethereal solution, which was separated from the potassium acetate, was well washed, dried, and fractioned. After the ether was distilled off, the thermometer rose rapidly to 200°, the greater quantity coming over between 215° and

240°. A considerable quantity of a black tar was left behind in the retort, which was not further examined. The presence of this, as well as the apparent formation of isobutyric acid, shows that, besides saponifying, the potash had also exercised a further action on the product. The fraction 215—240° was then redistilled, when the principal portion passed over at 217—223°, and gave on analysis the following result:—

I. 0·1435 gram substance gave 0·1568 OH_2 and 0·3629 CO_2.
II. 0·1254 „ „ 0·1370 „ 0·3165 „

	Found. I.	Found. II.	Theory for $C_{20}H_{42}O_4$.
C	68·97	68·83 per cent.	69·37 per cent.
H	12·14	12·14 „	12·14 „

This body has therefore the formula $C_{20}H_{42}O_4$, or 4H more than the body $C_{20}H_{38}O_4$, which should have been reproduced by the saponification. This new product is an almost colourless oil, having a peculiar odour, which does not resemble that of the aldehyde $C_{20}H_{38}O_4$. The first of the above combustions is from a fraction boiling between 217—219°, and the second from a fraction (219—223°). It therefore appears that by the saponification of the diacetate, the body $C_{20}H_{38}O_4$, probably first produced, is further acted on by the reducing and oxidising action of the potash, part being oxidised and part forming the body $C_{20}H_{42}O_4$.

The residue of the condensed isobutaldehyde left in the retort and boiling above 235° was distilled under a pressure of 100 mm. A considerable quantity came over between 185° and 200°; the next large fraction was between 220—235°. The distillation was discontinued when the temperature had reached 280°, and decomposition set in. No solid bodies were obtained. The portion boiling at 185—200° was then fractioned under the ordinary pressure, when it nearly all distilled over between 245° and 260°. This was then collected between every 5°; the principal product thus obtained boiled at 250—255°.

On analysis it gave the following results:—

I. 0·1234 gram substance gave 0·1231 OH_2 and 0·3328 CO_2.
II. 0·1370 „ „ 0·1374 „ 0·3666 „

	Found. I.	Found. II.	Theory for $C_{24}H_{44}O_4$.
C	73·55	72·97 per cent.	72·72 per cent.
H	11·08	11·14 „	11·11 „

It thus appears to have the formula $C_{24}H_{44}O_4$, and is probably produced according to the equation—

$$6C_4H_8O = C_{24}H_{44}O_4 + 2OH_2.$$

It is a stable body, and requires long boiling with dilute sulphuric acid to decompose it. Owing to the small quantity produced in the action of potash on isobutaldehyde, it could only be very little examined. It is an almost colourless oil, and distils at ordinary pressures without decomposition. It does not seem to combine with acid sulphite of soda. On heating with strong alcoholic potash, it turns black and is decomposed, forming a considerable quantity of a potassium salt. Two vapour-density determinations were made which gave 12·61 and 13·21.

The calculated density for $C_{24}H_{44}O_4 = 13·69$.

From these determinations, it appears evident that this body is much more stable than the lower condensation-products, as the figures obtained, although not agreeing well with the calculated ones, yet go to show that the body is produced by the condensation of six molecules of isobutaldehyde, the next lower one, $C_{20}H_{38}O_4$, having a calculated density = 11·82.

The fraction obtained between 220—235° under a pressure of 100 mm. was then carefully distilled under the same pressure. After repeating this operation several times, a considerable quantity was obtained, boiling constantly at 227—229°, which gave on analysis the following numbers:—

I. 0·1281 gram substance gave 0·1305 OH_2 and 0·3630 CO_2.
II. 0·1420 „ „ 0·1420 „ 0·4038 „

	Found. I.	Found. II.	Theory for $C_{28}H_{48}O_3$.
C	77·28	77·55 per cent.	77·77 per cent.
H	11·32	11·11 „	11·11 „

This body appears therefore to have the formula $C_{28}H_{48}O_3$. The formation may be expressed by assuming that four molecules of water are removed from seven molecules of isobutaldehyde according to the equation:—

$$7C_4H_8O = C_{28}H_{48}O_3 + 4OH_2.$$

This body is a very thick yellowish oil, having a very faint smell. It distils in a vacuum without decomposition, but at ordinary pressures it appears to split up into lower and higher boiling bodies, a tarry residue being left behind in the retort. This decomposition was also seen when two vapour-density determinations were attempted. By the Victor Meyer process in a lead-bath, they gave 10·42 and 10·77.

The calculated density for $C_{28}H_{48}O_3$ is 14·94.

The still higher-boiling condensation-products would be very difficult to obtain pure, and were not analysed. There appeared, however, to be a definite body boiling at about 250°, under a pressure of 100 mm. A table is appended of the bodies obtained and their boiling points.

$C_{12}H_{22}O_2$	154—157°	Condensation-products.
$C_{16}H_{30}O_3$ (?)	190—200°	
$C_{20}H_{38}O_4$	223—225°	
$C_{24}H_{44}O_4$	250—255°	
$C_{28}H_{48}O_3$	227—229° (100 mm. pressure)	
$C_{12}H_{26}O_2$	170—175°	Alcohol (and acetate) produced by the action of nascent hydrogen on $C_{12}H_{22}O_2$.
$C_{12}H_{24}O_2(C_2H_3O)_2$ ..	185—190°	
$C_{20}H_{37}O_4(C_2H_3O)$ ..	240—242°	Acetates produced by the action of acetic anhydride on $C_{20}H_{38}O_4$.
$C_{20}H_{36}O_4(C_2H_3O)_2$ ..	248—252°	
$C_{20}H_{42}O_4$	217—223°	Produced by saponifying $C_{26}H_{36}O_4(C_2H_3O)_2$.
$C_{12}H_{22}O_3$	245—255°	Acid produced by the action of potash on isobutaldehyde.

XI.—*The Alkaloïds of Nux Vomica.* No. II. *On Brucine.*

By W. A. Shenstone, Professor of Chemistry at Clifton College, Bristol.

In a former paper "On the Nux Vomica Alkaloïds" (*Chem. Soc. J.*, 1881), I showed that it is highly improbable that igasurine has any existence, and stated my intention of examining the two other alkaloïdal constituents by limited oxidation.

I have made a number of experiments with brucine by various methods, employing large quantities of material. I find that the action proceeds very rapidly to the production of oxalic and carbonic acids, especially with alkaline reagents. When such complete oxidation is prevented, the products are amorphous unworkable substances.

Strychnine behaves in much the same manner, but the action is not so rapid, and I may possibly return to this part of the subject in a

complete examination of strychnine, which the results given in this paper have induced me to undertake.

Strecker, Liebig, Gerhardt and Laurent, and others have reported experiments which have led them to suppose that brucine, when treated with dilute nitric acid, yields among other things either methyl or ethyl as nitrite or nitrate. I have not met with any corresponding statements concerning strychnine, and as the formula of brucine suggested that it might be a dimethoxyl-derivative of strychnine, I was led to make the experiments which I now report.

When brucine is heated in sealed tubes to 100° C. with several times its weight of strong solution of hydrochloric acid, it is not much affected. When, however, from 7 to 15 times its weight of the acid is employed, and the temperature is raised to 130—140°, on opening the tubes there is a great rush of a gas which is colourless, rather soluble in water, more so in alcohol, and not attacked in the cold by solid potassium hydrate.

This gas burns with a luminous green-edged flame giving clouds of hydrochloric acid, and when carefully freed from hydrochloric acid and passed through a red-hot tube, yields hydrochloric acid, which has been recognised by the ordinary reactions of that substance.

Although there was little doubt that the gas was methyl chloride, I thought it worth while to determine the amount of carbon dioxide produced by exploding a measured quantity of it with oxygen.

The gaseous contents of a tube in which brucine had been treated with large excess of acid were collected over mercury, and qualitative examination having shown that they consisted of a mixture of the gas in question with air, water-vapour, hydrochloric acid, and a little carbonic acid, the last three were removed, and a measured quantity of the mixture of air and chlorinated gas was exploded as usual with proper proportions of oxygen and air. The carbonic acid formed and the residual nitrogen were determined as usual. The following are the numbers (corr.) obtained. From them I calculated the volume of the chlorinated gas in the mixture examined, and so was able to know the relation between the gas burnt and the carbon dioxide which it produced:—

Vol. of chlorinated gas and air taken	=	5·77 c.c.
,, after adding air	=	28·83 ,,
,, ,, adding air and oxygen	=	49·22 ,,*
,, ,, exploding	=	41·18 ,,
,, ,, removing CO_2	=	36·68 ,,
,, of nitrogen after removing excess of oxygen	=	20·61 ,,

* The oxygen added contained 1·08 c.c. of nitrogen.

These numbers showed that 4·12 c.c. of the gas given off by brucine yielded 4·5 c.c. of carbon dioxide.

As 4·12 c.c. of ethyl chloride would have given 8·24 c.c. of carbon dioxide, this result leaves no doubt as to the nature of the gas in question. But as the excess of carbon dioxide is rather large, I may state that it is due to the following circumstance, which I think is not generally known:—

I find that on exploding a mixture of methyl chloride, oxygen, and air, the inside of the eudiometer becomes coated with a white solid, which is shown by the action of potassium hydrate to be mercurous chloride. This makes the tube rather opaque, and therefore, though I had no difficulty in observing where the liquid stood in the tube, I found it impossible to read the level of its surface with perfect exactness, and I was careful to read rather too high than too low.

When tubes containing strychnine and solution of hydrochloric acid in similar proportions to those employed in the experiments with brucine are heated, there is good evidence that the alkaloïd is much attacked, but little or no evolution of gas occurs. In an experiment in which 1 gram of strychnine was heated with 15 grams of acid for many hours at temperatures gradually rising to 170°, 7 c.c. only of gas were given off on opening the tube, and the air in the tube was found to contain carbon dioxide.

It is probable therefore that the difference in the formulæ of brucine and strychnine may be correctly accounted for by writing that of the former $C_{21}H_{20}(CH_3O)_2N_2O_2$, *i.e.*, strychnine, in which 2 atoms of hydrogen are replaced by 2 methoxyl-groups.*

In order to learn if the quantity of methyl chloride produced agreed with this hypothesis, I made the following experiments:—

(*a.*) 1 gram of dry brucine with 20 grams of acid heated to 160° for 7 hours, then to 180° for 7 hours, gave 64·6 c.c. at 0° and 760 mm.

(*b.*) 1 gram of dry brucine with 8 grams of acid heated to 140° for 6 hours, then to 160°, 180°, and 190° for 4 hours at each temperature, gave 70·7 c.c. of methyl chloride at 0° and 760 mm.

(*c.*) 1 gram of dry brucine with 15 grams of acid heated to 150°, 160°, and 170°, gave about 70 c.c. of methyl chloride.

(*d.*) 1 gram of dry brucine heated with 15 grams of acid to 145°

* In adopting the formula $C_{21}H_{22}N_2O_2$ for strychnine, I am aware that Claus and Glassner (*Ber.*, **14**, 773) have suggested that strychnine is a body of variable composition, containing sometimes 22 and sometimes 21 atoms of carbon in its molecule. After carefully reading their memoir, however, I have not felt that this hypothesis can be accepted until more exact results are brought forward, and some corresponding difference in property is established.

for 6 hours, then to 150° for 8 hours, and finally to 180° for 6 hours, gave 83 c.c. of methyl chloride at 0° and 760 mm.

(*e.*) As it appeared that prolonged heating at low temperatures gave the greatest yield of methyl chloride, I employed in this final experiment the lowest temperature that seemed likely to answer, and continued the application of heat for longer periods than in the previous experiments. 1 gram of dry brucine heated with 15 grams of acid for 14 hours to 135°, then for 13 hours to 145°, then to 150° for 7 hours, and finally to 160° for 7 hours, gave 90·2 c.c. of methyl chloride at 0° and 760 mm.

At 0° and 760 mm. 1 gram of dimethoxystrychnine would theoretically yield 113 c.c. of methyl chloride. Each of my experiments gave more than half that volume, none of them gave more than that amount, and, under the most favourable conditions (Experiment *e*), I obtained, as will be seen, 79 per cent. of the theoretical yield.

The non-gaseous contents of the tubes after heating were black, sometimes rather tarry liquids; these, on slight dilution, gave a precipitate which was soluble in pure water. Alkalis precipitated a base from its solution which underwent instant change on exposure to the air; the base formed an insoluble platinum salt which also was too unstable for examination. As strychnine is also profoundly attacked by hydrochloric acid, I am not inclined to regard this base as likely to be the compound $C_{21}H_{18}N_2O_2$, but rather in all probability a product of further change; and this opinion is confirmed by the fact that it does not appear to be affected by nascent hydrogen, which might be expected to convert the compound $C_{21}H_{18}N_2O_2$ into strychnine or an isomeride of strychnine.

As there was no hope of obtaining results of value with this substance, I decided to try the effect of hydriodic acid on brucine at somewhat lower temperatures. My results are worth a brief record, but are not conclusive. When brucine or its hydriodide is heated gradually up to 100° with eight times its weight of solution of hydriodic acid (sp. gr. 1·9), and maintained at that temperature for two hours, a black solid separates, from which hot dilute hydrochloric acid extracts a new base. A further quantity of the same base remains in solution. When precipitated by alkalis it at once undergoes very rapid oxidation. On evaporating an acid solution of the hydrochloride in a vacuum over sulphuric acid it is also destroyed Addition of solution of iodine in potassium iodide threw down the periodide as a chocolate powder, with a slight odour of iodine when damp. This appeared to be permanent at first; but over sulphuric acid it continued to lose weight steadily, although very slowly after

the first day or two. When this substance was placed in a vacuum over sulphuric acid, the loss was much increased for the first few hours, and then continued pretty steadily for some days. I was proceeding to analyse it in the hope that the change of weight was due only to the loss of small quantities of iodine, but I found, on treating it with solution of sulphur dioxide, that the solution obtained had a distinctly brown tint at once, and as such a change of colour had been previously found to accompany the oxidation of the base, I unwillingly concluded that even in this combination it had not altogether escaped change, and that no value could be attached to quantitative results obtained with it.

The base may be easily recognised by a very fine colour-reaction. If ammonia is added to an acid solution of it, and this is at once extracted with chloroform, the solution in chloroform leaves on evaporation a greenish solid which dissolves in solution of hydrochloric acid with a fine coloration, blue when seen in thin layers, purple in thicker layers. The colour of the solution remains unchanged for many days.

I present these somewhat imperfect results to the Society now, because I have come to the conclusion that it will in future be most profitable to continue my endeavours to make out the nature and relation between the Nux vomica alkaloïds by an examination of strychnine. My present results show that there is reason to think that brucine is a dimethoxyl-derivative of strychnine. The removal of these methoxyl-groups gives rise to bodies of such unstable character, that for the present their further examination seems less likely to repay the labour they demand than experiments made upon strychnine, which may very probably yield more manageable products.

XII.—*The Behaviour of the Nitrogen of Coal during Destructive Distillation; with some Observations on the Estimation of Nitrogen in Coal and Coke.*

By William Foster, M.A., Lecturer on Chemistry at the Middlesex Hospital.

When coal is submitted to destructive distillation in close vessels, as in coal-gas manufacture, ammonia-gas with numerous other substances is evolved. It is usual for writers on the subject to consider that the greater portion of the nitrogen of coal takes the form of ammonia-gas or its compounds. Professor Roscoe in his small manual has the following sentence:—"Coal contains about 2 per cent.

of nitrogen which, when the coal is heated in close vessels, mostly comes off in combination with the hydrogen of the coal as ammonia."

The experiments which I now bring before the Society have been made with the view of determining to what extent the nitrogen of coal is converted into ammonia during destructive distillation. Only a small fraction of the whole quantity of nitrogen is obtained as ammonia. Some nitrogen appears as cyanogen; some is presumably present in the coal-gas in the elementary condition, while a considerable portion remains behind in the coke.

One particular sample of Durham coal has been employed in these experiments. It is a kind in favour with certain metropolitan gas engineers, who are fairly well acquainted with its ammonia-producing capabilities. The results of the ultimate analysis of this sample are expressed by the following numbers:—

Carbon	84·34
Hydrogen	5·30
Nitrogen	1·73
Sulphur	0·78
Oxygen (by difference)	4·29
Moisture lost at 212° F.	1·14
Ash	2·42
	100·00

On heating it in a close platinum crucible until gas ceased to come off, the following numbers were obtained:—

Volatile matter	25·54
Coke	74·46
	100·00

The coke obtained in this way was reserved and its nitrogen estimated.

The observations made may be classed as follows:—

Estimation of the total nitrogen in the coal.

Estimation of the amount of nitrogen which is evolved as ammonia during destructive distillation.

Estimation of the amount of nitrogen evolved as cyanogen during destructive distillation.

Estimation of the amount of nitrogen which remains behind in the coke.

Estimation of the Total Nitrogen of the Coal.

Three methods in use for this purpose have been employed—that is (1) by heating with excess of soda-lime; (2) by heating with excess

of copper oxide in an atmosphere of carbonic anhydride; and (3) by heating with an excess of copper oxide *in vacuo*.

Soda-lime Method.—In these cases the ammonia evolved was received in hydrochloric acid, converted into the platinum-ammonium chloride, dried, and weighed. The last two experiments were as follows:—

Coal taken in grams.	Platinum-ammonium chloride obtained in grams.	Nitrogen obtained in grams.	Nitrogen percentage of coal.
2·339	0·629	0·03940	1·684
1·349	0·368	0·02305	1·708
		Mean	1·696

Copper Oxide Method (in an Atmosphere of CO_2).—Three successful experiments by this method gave 2·01, 2·03, and 1·90 respectively as the nitrogen percentages; but as the carbonic anhydride was obtained from marble and hydrochloric acid in the usual way, the uncertainty arising from the presence of small quantities of air in the carbonic anhydride from this source renders it undesirable to employ the results obtained by this method in the present inquiry.

Copper Oxide Method (in vacuo).—These experiments were of the ordinary character, rough copper oxide being employed. The last three gave the following results:—

Coal taken in grams.	Nitrogen obtained in c.c. (uncorrected).	Nitrogen obtained in grams.	Percentage of nitrogen in coal.
0·534	8·4	0·00976	1·83
0·532	8·0	0·00936	1·76
0·559	8·0	0·00952	1·70
		Mean	1·763

The Estimation of the Amount of Nitrogen which is Evolved as Ammonia during Destructive Distillation.

The process of coal-gas manufacture has been carried out on a small scale. A weighed quantity of the coal was placed in a combustion-tube sealed at one end, the outlet being connected with an arrangement containing hydrochloric acid for washing the coal-gas. In this way the whole of the ammonia was absorbed from the coal-gas. At the close of the operation the acid liquor was removed, the tar was washed with warm acidulated water, and the ammonia recovered from the mixed acid liquors by distillation with caustic soda. The ammonia was eventually converted into the double platinum-ammonium chloride, dried, and weighed.

Coal taken in grams.	Platinum salt obtained in grams.	Nitrogen obtained in grams.	Percentage of nitrogen of coal evolved as ammonia.
39·97	1·534	0·0961	0·251

The quantity of ammonia obtained in this experiment is a little higher than that obtained in the commercial way from this description of coal.

Estimation of the Amount of Nitrogen evolved as Cyanogen during Destructive Distillation.

After the coal-gas produced in the preceding experiment had been freed from ammonia, it was made to pass through a combustion-tube containing slaked lime kept at a high temperature by means of an external source of heat. In this way the cyanogen was decomposed, with production of a certain quantity of ammonia, which was absorbed by means of hydrochloric acid placed in suitable apparatus at the outlet. The ammonium chloride was converted into the platinum salt, dried, and weighed.

Coal taken in grams.	Platinum salt obtained in grams.	Nitrogen obtained in grams.	Percentage of coal evolved as cyanogen.
37·97	0·166	0·0104	0·027

Estimation of the Amount of Nitrogen which remains behind in the Coke.

Some observations on this subject by myself were made at the last Annual Meeting of the Gas Institute, and are published in its Transactions for 1882. Since that meeting attention has been directed to the matter by several gentlemen well known in the gas world. Dr. Siemens alludes to it in his recent address at Southampton.

The specimen of coke used was a mixture of two portions obtained in two distinct operations. One was that produced by heating the coal in a close platinum crucible until gas ceased to come off; the other was the coke taken from the combustion-tube in the experiment on destructive distillation. The two were well mixed and ground to a very fine powder in an agate mortar. The nitrogen present was estimated firstly by ignition with soda-lime, and secondly by ignition with copper oxide *in vacuo*.

Soda-lime Process.—The following are the last two experiments made:—

Coke taken in grams.	Platinum salt obtained in grams.	Nitrogen obtained in grams.	Percentage of nitrogen in coke.
1·805	0·337	0·0211	1·16
1·826	0·342	0·0214	1·17
		Mean.....	1·165

Copper Oxide Process (*in vacuo*).—The last three experiments made were as follows:—

Coke taken in grams.	Nitrogen obtained in c.c. (uncorrected).	Nitrogen obtained in grams.	Percentage of nitrogen in coke.
0·510	4·0	0·0047320	0·928
0·547	5·8	0·0068266	1·240
0·636	6·2	0·0071858	1·130
		Mean	1·099

A general consideration of these two methods of estimating nitrogen leads one to infer that higher numbers would be obtained by combustion with copper oxide *in vacuo* than by similar treatment with soda-lime; and such results are shown in the experiments on the coal. The results obtained with the coke are somewhat irregular, the mean not being in accordance with what was anticipated. However, the conditions best for an experiment were not realised at the time. From six to eight hours' steady and continuous heating of the charge is necessary for complete decomposition; and in the case of experiments in which the mercury pump has been used, it has been found advisable to maintain the pressure inside the combustion-tube as near that of the atmosphere as possible, until the decomposition of the charge has been complete. The gaseous products in the tube have then been quickly and completely removed. With copper oxide *in vacuo* much advantage has been derived by placing the combustion-tube in an outer tube of wrought iron, just sufficiently wide and long enough to encircle it the whole length of the highly heated part. For every cubic centimetre of nitrogen obtained there have been from 100 to 150 c.c. of carbonic anhydride to be dealt with. With the quantities of coal and coke operated on, large quantities of copper oxide in wide tubes have been used, and when the latter have been enclosed in an iron tube, the charges have been worked off with ease. Bursting of the combustion-tube has not only not occurred, but a ready and efficient control over the temperature of the charge has been maintained.

Having regard to the coal, the mean of the results of the soda-lime process is 1·696, and with copper oxide *in vacuo* the mean is 1·763. I have taken 1·730 as the percentage of nitrogen in the coal. The experiments on the coke with soda-lime furnish a mean of 1·165, and

with copper oxide *in vacuo* a mean of 1·099. I have taken 1·132 as the nitrogen percentage of the coke.

A summary of the results thus far obtained may be classed as follows:—

Percentage of nitrogen in the coal	1·730
Percentage of nitrogen of coal evolved as ammonia during destructive distillation	0·251
Percentage of nitrogen of coal evolved as cyanogen during destructive distillation	0·027
Amount of nitrogen remaining in coke furnished by 100 parts of coal	0·842
	1·120
Nitrogen from 100 parts of coal unaccounted for, the larger portion of which is presumably present as free nitrogen in the coal-gas. Some is no doubt in the tar	0·610

If we further reduce these figures to percentages on 100 parts of nitrogen, their relation to each other becomes more intelligible:—

Nitrogen of coal evolved as ammonia	14·50
Nitrogen of coal evolved as cyanogen	1·56
Nitrogen of coal present in the coal-gas in the elementary condition	35·26
Nitrogen remaining behind in the coke	48·68
	100·00

I have not made any experiments on the amount of nitrogen in the tar, nor am I in possession of any information on the subject. I have assumed that the quantity is relatively small.

Some lengthy observations have been made on the production of ammonia at stated intervals during the period of destructive distillation. They are being published in the *Journal of Gas Lighting*. It appears from the results obtained, that the coal-gas is richest in ammonia during the middle of the period and poorest at the close; in fact, the poverty of the coal-gas (so far as ammonia is concerned) at the close of the process of distillation is very marked.

XIII.—*Preliminary Note on some Diazo-derivatives of Nitrobenzyl Cyanide.*

By W. H. Perkin, Ph.D., F.R.S.

Some time since, while making some experiments with benzyl compounds, I prepared nitrobenzyl cyanide, not knowing that it had already been examined by Radziszewsky (*Ber.*, **3**, 198). It was treated with alcoholic potash to see whether, like benzonitrile, it would yield its acid, nitrophenylacetic acid. In making this experiment, I was very much struck with the remarkable action of this reagent upon it, an intense crimson colour being produced. This colour, however, soon becomes of a brownish-purple, and after a time changes to a dirty greenish-blue. This peculiar action of alkalis on nitrobenzyl cyanide has already been noticed by Czumpelik (*Ber.*, **3**, 474). From the intensity of the colour developed in this reaction, it appeared to me that some definite body must be produced, and as I was curious to get an idea of its nature, it was thought that it might perhaps form some compounds with diazo-compounds, and on trying this, the following results were obtained:—

An alcoholic solution of nitrobenzyl cyanide was mixed with some alcoholic potash, and directly after an aqueous solution of diazobenzene chloride was added until the crimson changed to a yellowish colour. The mixture, which contained a brown precipitate, was further diluted, the solid product collected on a filter, washed and purified by crystallisation from alcohol, and then from glacial acetic acid. In this way a substance was obtained, crystallising in orange-yellow needles; under some conditions, however, it is deposited as an orange-red crystalline powder. It melts at 201—202°, and on analysis gave numbers corresponding with the formula $C_{14}H_{10}N_4O_2$.

Its alcoholic solution gives with alkalis a compound which is of a beautiful violet colour; this colour disappears on the addition of an acid.

The constitution of this body has not yet been fully worked out, but it appears to be analogous to the compound lately described by Tiemann, viz., the phenylaniloacetic nitril with the diazo-group in place of C_6H_5HN, thus—

$C_6H_5.CH(NHC_6H_5).CN.$

Phenylaniloacetic nitril.

$C_6H_4NO_2CH(N{=}NC_6H_5)CN.$

The formation of this body is apparently analogous to that of

azonitro ethylphenyl from sodium-nitroethane and a diazobenzene salt described by Victor Meyer and Ambuli (*Ber.*, 8, 781, 1073).

Other diazo-compounds also combine with nitrobenzyl cyanide, and the further study of these compounds is being carried on. Endeavours are also being made to introduce other than diazo-radicals.

When preparing the ordinary nitrobenzyl cyanide, which appears to be the para-compound, I obtained a second body fusing at about 45°, which no doubt will prove to be orthonitrobenzyl cyanide.

XIV.—*Researches on the Induline Group.* (Part I.)

By Otto N. Witt, Ph.D., F.C.S., and Edward G. P. Thomas.

The term "Induline" is applied in commerce to a series of violet and blue dyes, less brilliant than the majority of artificial colouring matters, but distinguished by great fastness to light and atmospheric influences. Scientifically, the term may be applied to all coloured compounds formed by the action of amidazo-compounds on the hydrochlorides of aromatic amines, with elimination of ammonia. Some of them may be obtained by other well-known processes, which need not be mentioned here, as the object of this paper is to lay before the Society an account of our researches on the formation of amidazobenzene and its action on aromatic hydrochlorides.

These researches were begun in January, 1876, and continued, with occasional interruptions, up to the present time. They have been partly embodied in the specifications of certain patents, which we have taken out in different countries.

It has long been known that amidazobenzene, treated with aniline hydrochloride or nitrate, produces a dark-blue coloration; but as far as we have been able to ascertain, this reaction had not been carefully investigated, or turned to practical account until we began to study it. This was probably due to the supposed impossibility of producing the necessary quantities of amidazobenzene. Our efforts to overcome this difficulty resulted, however, in an easy method of preparation—a method which was discovered independently in 1878 by Mr. Grässler, of Cannstatt.

In studying the action of amidazobenzene on aniline hydrochloride, we soon found that it was much more complicated than was generally supposed. Hofmann and Geyger (*Ber.*, 1872, 5, 474), who studied this action in 1872, state that only one dye-stuff is formed simul-

taneously with ammonium chloride, and they represent its formation by the formula

$$C_{12}H_{11}N_3 + C_6H_7N = C_{18}H_{15}N_3 + NH_3.$$

Although we have varied the conditions of our experiments in every possible way, we have been unable to effect so simple and complete a transformation. We have observed on the contrary :—

I. That the reaction invariably results in the formation of several colouring matters, differing from each other both in composition and in properties.

II. That the nature of the products formed, as well as the quantities in which they are obtained, are largely dependent upon the temperatures at which the reaction takes place, and the manner in which it is conducted.

In the present paper we purpose to confine ourselves to a description of those compounds which we have obtained in a state of purity, as well as of their mode of preparation, leaving it, we hope, to a subsequent communication to explain their constitution, and establish a theory of the whole reaction.

Most of these compounds have acquired importance as commercial products. In order to avoid confusion and new names, we shall retain the commercial designation for the pure substances.

The following is our

Process for the Production of Indulines on the Large Scale.

We first prepared diazamidobenzene by one of the well-known processes for the production of that body. If properly prepared, it consists of a granular crystalline substance of yellow colour, which becomes brownish on drying. In order to transform it into amidazobenzene, we first tried the method indicated by Kekulé ("Benzolderivate," p. 206), but we soon found that it was quite useless for our purpose. Alcohol, in this, as in most cases where diazo-compounds are to be dealt with, proved most detrimental to the reaction. We therefore tried other solvents, and found that aniline was by far the best. It has the advantage of being an excellent solvent for both diazamidobenze and aniline hydrochloride, and this greatly facilitates the reaction of the two substances.

If a mixture of 2 parts diazamidobenzene, 1 part aniline hydrochloride, and 4 parts aniline be left at a gentle heat for 24 hours, not a trace of nitrogen is formed, but the whole of the diazo-compound is transformed into amidazobenzene. The latter may be separated by treating the mixture with sufficient hydrochloric acid and water to dissolve all the aniline. Crude hydrochloride of amidazobenzene settles out in bluish glistening needles, and may be collected and

washed with dilute hydrochloric acid. From this crude salt a pure substance may be prepared by washing with dilute ammonia, which frees the base. The latter is dissolved in pure boiling benzene. On cooling, fine yellow crystals settle out, which consist of a molecular combination of amidazobenzene with benzene. On drying, the benzene is driven off, whilst pure amidazobenzene remains in the form of a brilliant yellow powder. On recrystallisation from alcohol, it is obtained in magnificent orange prisms having a blue reflex, and melting at 125—126°.

Another process consists in basifying the mixture of aniline, amidazobenzene, and aniline hydrochloride by means of caustic soda, washing with water, and drawing off the aniline with steam. Crude amidazobenzene then remains in the still, and may be purified by dissolving it in spirit, adding hydrochloric acid, collecting the crude hydrochloride which settles out on cooling, and treating it as above described.

Amidazobenzene was formerly tried as a yellow dye-stuff, but abandoned on account of the difficulty then experienced in its production, and its sensitiveness to mineral acids. Recently, however, it has become an important article of manufacture, Grässler having shown that its sulpho-derivatives are excellent yellow dyes, not too sensitive to mineral acids.

For the production of the different indulines, it is not necessary to separate the amidazobenzene from the liquid in which it was formed. This liquid, besides the amidazobenzene, consists, as already stated, of aniline and the whole of the aniline hydrochloride originally used. This aniline hydrochloride reacts upon the amidazobenzene formed, if the temperature of the mixture be raised, and the free aniline present facilitates and moderates the reaction. According to the quantity of aniline and aniline hydrochloride present, and especially to the temperature at which the reaction takes place, the products obtained differ in their properties and composition. If the mixture referred to be heated for 24 hours on the water-bath, and below the temperature at which there is any formation of colour, it deposits an abundant crystallisation of a compound which is not an induline, but which, in the formation of indulines, seems to play so important a part that it cannot be passed over in silence. To prepare this substance in the pure state, it is sufficient to mix the mass from which it partly separates with strong spirit, and filter off the brown crystalline precipitate from the mother-liquor. After washing with spirit and water, the precipitate is dissolved in boiling aniline, from which, on cooling, it settles out in beautiful garnet-coloured leaflets. These, after filtering and washing with boiling spirit, are quite pure and fit for analysis.

	Calculated for $C_{36}H_{29}N_5$.	Obtained. I.	Obtained. II.
C	81·35	81·59	81·06
H	5·46	6·81	5·93
N	13·18	—	—

The melting point of this substance is 236—237°. It dissolves in concentrated sulphuric acid with violet coloration, which, on heating to 300°, suddenly becomes sky-blue. The solution, if mixed with water, exhibits a fine crimson fluorescence.

These reactions show that the substance is identical with that described by one of us as being one of the products of decomposition of diphenylnitrosamine (O. N. Witt, *Ber.*, **10**, 1877, p. 1311).

On studying the reactions of this compound, we were struck by their similarity to those of the body described by Kimich (*Ber.*, **8**, 1875, p. 1028), under the name of *azophenine*, and obtained by heating nitrosophenol with aniline acetate. Kimich, however, attributes to his substance the formula $C_{36}H_{29}N_5O$. He recrystallised it from toluene and xylene, which, as we have convinced ourselves, are incompetent to effect complete purification. We therefore conjectured the identity of Kimich's substance with our own, and, to verify the supposition, prepared azophenine according to Kimich's method from nitrosophenol. We found that on using aniline acetate, a very small yield of an impure substance was obtained; whereas on heating nitrosophenol with aniline hydrochloride for 24 hours on the water-bath, an abundant yield of azophenine was the result. This, purified by the process described, gave a substance free from oxygen, and in every respect identical with our own.

Azophenine from Nitrosophenol.

	Calculated for $C_{36}H_{29}N_5$.	Obtained. I.	Obtained. II.
C	81·35	81·81	81·06
H	5·46	6·25	6·81
N	13·18	—	—

It follows, therefore, that Kimich's azophenine was an impure substance. We propose, however, to retain for the purified product Kimich's name azophenine, and we will henceforth so call the body $C_{38}H_{29}N_5$. On reduction with tin and hydrochloric acid, azophenine gives a mixture of several bases, amongst which we have been able to identify aniline and paraphenylene-diamine. On heating it with paraphenylene-diamine hydrochloride in presence of aniline, it quickly disappears, yielding a violet melt. Heated with metaphenylene-dia-

mine hydrochloride, under the same conditions, it also disappears with production of a blue melt.

The mother-liquors from the preparation of azophenine, by means of amidazobenzene contain, besides aniline, aniline hydrochloride and spirit, considerable quantities of ammonium chloride, paraphenylenediamine hydrochloride, and small quantities of a dichroïc green and red substance, which we have not analysed.

If after heating the mixture of aniline, aniline hydrochloride, and amidazobenzene on the water-bath, as above described, the temperature be raised to 125—130°, all trace of azophenine disappears; the melt soon turns blue, and after 12 hours no more induline is formed. It is then removed from the flame and cooled down very slowly. Under these conditions a crystalline deposit is formed, which may be separated by filtration and washing with spirit, in which the crystalline compound is almost insoluble.

The mother-liquor and spirit washings contain induline B hydrochloride. This compound is very soluble in spirit, a little soluble in water, easily soluble in a concentrated aqueous solution of aniline hydrochloride. Its base dissolves in spirit with a brown-red colour. Its sulpho-derivative is insoluble in water, and forms salts which, if quite neutral, dissolve in water with a reddish-blue coloration. On adding an alkali, the solution turns red. From the acidulated solutions, the colouring matter is totally absorbed by silk, whilst it has little or no affinity for cotton.

The crystals collected on the filter are not yet pure. They contain considerable quantities of ammonium chloride, which is removed by thorough washing with boiling water. The remaining colouring matter may then be recrystallised from alcoholic hydrochloric acid, or from a mixture of aniline and aniline hydrochloride, from which it is obtained in glistening brown leaflets, insoluble in cold, soluble in hot spirit, very soluble in aniline. This substance we call *Induline* 3B. The following results were obtained on analysis:—

	Calculated for $C_{30}H_{23}N_5HCl$.	Obtained. I.	II.	III.
C	73·54	73·57	74·16	73·81
H	4·90	5·29	5·54	5·48

On treating the substance with alcoholic sodic hydrate, the free base was obtained. To remove chloride of sodium, it was washed with water, dissolved in a large quantity of spirit, then filtered, and the spirit was distilled off, until a very concentated solution was obtained. From this solution the free base gradually settled out in

black warty crystals which, after drying at 120°, gave on analysis the following numbers:—

	Calculated for $C_{30}H_{23}N_5$.	Obtained. I.	II.	III.	IV.	V.	VI.
C	79·46	80·13	80·02	79·91	79·95	—	—
H	5·08	5·42	5·37	5·33	5·42	—	—
N	15·05	—	—	—	—	15·64	15·10

If the drying of the base at 120° be omitted, it always contains some alcohol, which is not given off even after prolonged standing over sulphuric acid. This is shown by the following numbers:—

	I.	II.	
C	78·34	78·27	—
H	5·63	5·51	—
Loss on drying at 120° C. ..	—	—	2·36

obtained with a substance which had been dried for a fortnight at the ordinary temperature. Curiously enough the quantity of alcohol retained corresponds with a molecular proportion, as may be seen by the numbers calculated for the formula $4C_{30}H_{23}N_5 + C_2H_6O$.

C	78·79
H.....	5·27
Alcohol ..	2·53

Induline 3B is of a sky-blue shade; its free base dissolves with a purple coloration in spirit and aniline. By treating it with strong sulphuric acid, it is transformed into a sulpho-derivative, the properties of which are similar to those of induline B. The shades produced by it on silk and wool are much bluer; it has a slight affinity for cotton, and is consequently used in calico printing for the production of delicate fast greys.

Referring again to the original mixture of diazamidobenzene, aniline, and aniline hydrochloride, if the proportion of the latter be increased and the temperature maintained at 165—170°, only small quantities of induline 3B will be formed, and another substance will be found to crystallise out of the melt. This is induline 6B. The best method of preparation consists in heating a mixture of

100 parts amidazobenzene,
130 ,, aniline hydrochloride,
300 ,, aniline,

for four or five hours at 110°. After that time other 65 pts. aniline hydrochloride are added, and the mixture is then heated to 165—170° for 24 hours.

From this melt the induline 6B is deposited on cooling in brilliant green crystals, which may be separated from the bye-products in the same manner as in the case of the 3B. The hydrochloride of induline 6B is apt to lose hydrochloric acid if in contact with water or alcohol. It should therefore, before being subjected to analysis, be boiled with pure hydrochloric acid, or treated with hydrochloric acid gas and dried over quicklime. A product treated in this manner gave on analysis the following numbers:—

	Calculated for $C_{36}H_{27}N_5.HCl$.	Obtained. I.	II.	III.
C	76·39	75·52	76·29	75·98
H	4·77	4·94	5·24	5·18

From this hydrochloride the free base may be obtained by treating it with alcoholic soda solution, washing with water, and crystallising from aniline. From this solvent it is obtained in brilliant green needles of a beautiful metallic lustre. On combustion it gives numbers which correspond with the formula $C_{36}H_{27}N_5$.

	Calculated for $C_{36}H_{27}N_5$.	Obtained. I.	II.	III.
C	81·04	81·09	81·09	—
H	5·12	5·90	4·71	—
N	13·23	—	—	13·07

From these numbers it will be seen that induline 6B differs only slightly from azophenine in composition; nevertheless it is very different in its properties. The solution of induline 6B base is of a dark bluish-purple colour; the hydrochloride is insoluble in all the usual solvents, even aniline dissolving very little of it. It is moderately soluble in phenol and in concentrated sulphuric acid, with an intense greenish-blue shade, which becomes even greener by artificial light. The solution in sulphuric acid on being heated gives rise to the formation of sulpho-acids, the salts of which are brought into commerce as a valuable blue dye.

The mode of formation of all these compounds is too complicated to allow of an easy and simple explanation of the reaction in which they originate, especially so long as their *constitution* remains what it now is, a mystery. Although it must be admitted that the higher indulines, and especially induline 6B, are the products of transformation of azophenine and induline B; still it is clearly shown by our researches that this transformation is not a mere phenylation, as might be inferred from a comparison of our induline process with the rosani-

line-blue process. No doubt a phenylation takes place, as is proved by the presence, at an early stage, of ammonium chloride in all its melts, but there are other more complicated condensations taking place at the same time. It is our firm conviction that these condensations are due to the dehydrogenating action of amidazobenzene. This action, as shown by one of us in a previous paper, although slow and quiet, is still very powerful. The best proof of our assumption is the presence of one of the reduction-products of amidazobenzene, viz., paraphenylene-diamine, in all induline melts, and at every stage of the process.

It is quite clear that so oxidisable a compound as paraphenylene-diamine does not long remain intact in the melt; as soon as it is formed, it undergoes transformation, and probably enters into the molecule of the indulines produced.

Our view is further supported by the fact that, in order to obtain an induline melt of a given shade, it is much more important to choose the proper base than the proper azo-compound. Thus in the melt which we have described, azobenzene, and even amidazonaphthalene, may replace the amidazobenzene without materially altering the result, which is always a blue dye of the induline character. But if instead of aniline, orthotoluidine or naphthylamine be treated with its own hydrochloride and amidazobenzene, the result is totally different, red colouring matters being the products of these reactions.

Our researches on these points are not yet completed, the practical work being attended with considerable difficulty; neither does it admit of a rapid determination of the products of a given reaction. Still we hope at some future time to be able to lay before the Society new and more definite results.

XV.—*On a New Method of Estimating the Halogens in Volatile Organic Compounds.*

By Richard T. Plimpton, Ph.D., and E. E. Graves.

The method now almost exclusively adopted for the determination of the halogen elements in organic compounds is that of Carius, which consists, as is well known, in heating the substance to be analysed in a sealed tube with fuming nitric acid and silver nitrate.

This method, although in many respects an excellent one, is open to certain objections. Amongst these are, the risk which attends experiments with pressure tubes, the uncertain period during which the

tube must be heated to ensure complete decomposition, and the semi-molten condition in which the precipitate is often obtained, rendering it difficult to wash out the last traces of silver nitrate. The only other process which has been much used is that of heating the substance to a high temperature, in a combustion tube filled with quick-lime, dissolving up the contents of the tube with dilute nitric acid, and precipitating with silver nitrate. But certain compounds, like chlorobenzene, are only with difficulty decomposed by hot lime; further, the operation of dissolving so large a quantity of lime is objectionable, and either for these reasons, or because of the necessity of using lime free from chlorine, which is not always at hand, the method has fallen into disuse.

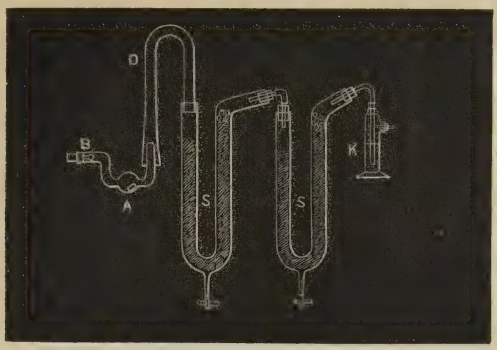
J. Volhardt (*Annalen*, **190**, 40) describes a method which has been worked out by Feez, Schraube, and Burckhardt, in which the substance is burnt in a covered porcelain crucible, with a mixture of sodium carbonate and potassium nitrate, or, if a more volatile compound, with the same mixture in a tube. No analyses of very volatile compounds were, however, made. According to Schiff (*Annalen*, **195**, 293) a very similar process was recommended long ago by Piria, who used two platinum crucibles, the smaller of which, after receiving the substance to be analysed, was filled up with black flux, inverted, and placed within the larger, the ring-shaped space between the two crucibles being then filled with the same compound. Schiff, who substituted for the black flux sodium carbonate, or a mixture of the same with lime, obtained excellent results with solid bodies, and even with some liquids; certain other liquids, however, always partially escaped decomposition.

In the method now to be described, we have used an entirely different means of decomposing the organic substance, namely, by introducing it in the state of vapour into the flame of a Bunsen burner, where the halogens are obtained chiefly in combination with hydrogen, and in small quantity in the free state. The products of combustion are drawn through suitable absorbers containing sodium hydrate, and the halogens so collected are then estimated in the usual way.

After many trials we adopted the form of apparatus shown on p. 121. It consists of a burner (A), easily made from a hard glass bulb tube, and bent as shown in the figure. At B there is the usual Bunsen arrangement for mingling gas and air, and the jet and air-holes are of such a size that with the full pressure of gas, a flame of about three-quarters of an inch in length is obtained. The external diameter of the tube is about $\frac{7}{16}$ inch, and it is contracted at the orifice to $\frac{1}{4}$ inch.

The flame is placed within the conical tube (D), by which the products of combustion are conveyed to the scrubbers (S) (S). Diameter

of tube at widest part, $1\frac{5}{8}$ inch, tapering in 4 inches to $\frac{3}{4}$ inch; length of tube from junction with the scrubber to top of bend, 6 inches.



The scrubbers consist of two **U**-tubes of the form shown, fitted with draining tubes closed by clips, and filled with glass beads. The beads used were in the form of $\frac{1}{8}$-inch lengths of quill tubing, and were easy to wash. A few large round beads were placed at the top, to keep the others in place. The tube (D) is fitted into the scrubber by means of a ring of india-rubber, and the corks are of the same substance. The dimensions of the **U**-tubes are: diameter of tube, 1 inch; length of short limb, 10 inches; length of inclined tube, 4 inches; width across, 4 inches.

K is a small bottle containing solution of silver nitrate, and serves to indicate the completeness of the absorption, and the rate of the current. It is connected with a Sprengel pump (water). A small weighing tube is required, of such a size that it will easily slide down the burner into the bulb. It must be stoppered, but not contracted at the mouth, otherwise its contents will not readily flow out into the bulb.

The mode of conducting an experiment is the following: the scrubbers are charged with 50 c.c. each of a solution of pure caustic soda, prepared by dissolving 1·5 grams of sodium in 100 c.c. of water, and a current of air is drawn through the apparatus, just sufficient to allow of the Bunsen flame burning steadily within the conical tube. A disc of card may be placed round the burner, so as nearly to close the mouth of the cone, to neutralise the effects of draughts. The liquid to be analysed is then weighed out in the small stoppered tube (0·1—0·25 gram), and the gas having been previously turned on for some seconds, the weighing tube is quickly unstoppered, and dropped down the burner, the gas instantly lit, and the flame placed within the cone. If the liquid has not already run out into the bulb, it is made

to do so, and its evaporation is then aided by warming the bulb with hot water, or otherwise. The temperature of the bulb is raised or lowered, so that the presence of the substance may always be detected in the flame, and yet not in sufficient quantity to cause the flame to become luminous. With some bodies the flame is tinged green; with others, *e.g.*, amyl chloride, a slight luminosity at the tip of the flame is all that is perceptible. The success of the experiment depends upon the regular volatilisation of the compound; on the one hand this must not be unduly hurried, or the flame becomes luminous, and the combustion may be incomplete; on the other, the evaporation should not be too slow, or, before it is complete, the soda in the absorbers will have become carbonated, and therefore incapable of stopping every trace of the free halogen and their acids. The silver nitrate solution will of course indicate when this point has been reached.

Usually the combustion occupies 15—20 minutes, and the silver solution remains clear. As soon as the liquid has disappeared from the bulb and tube, the former is warmed gently with a Bunsen burner, and then more strongly, so as to drive off the last traces.

We have found that the easiest way of securing a slow and regular evaporation in the case of liquids boiling below 100° C., is to place the stoppered weighing tube *with* its stopper within the bulb; on warming with hot water, sufficient vapour escapes round the stopper. This plan was adopted with good results in experiments made with carbon tetrachloride, 76°; ethyl iodide, 71°; ethyl bromide, 39°; and ethylene chloride, 82°. In the case of ethyl iodide, indeed, it is impossible to use an open tube, for the iodide is so little inflammable and so volatile that the gases refuse to burn at all.

Liquids with boiling points between 100° and 135° are weighed out in a tube from which the stopper is removed on dropping it into the burner. The most convenient way of heating the bulb is to surround it with water kept hot by a current of steam.

With liquids boiling above 135° cautious heating with a Bunsen may be resorted to; the flame must be kept moving, and taken away directly the substance shows its presence in the flame. When the combustion is at an end, the soda-solution is run out from the **U**-tubes into a flask of about a litre capacity, and the wash-water from the same, together with the rinsings of the corks and connecting tubes, added. Generally the total quantity of liquid amounts to about half a litre. Some sulphurous acid is now added, and the contents of the flask boiled down for 10 minutes or more over a large Bunsen, so as to reduce any chlorates, &c., that may have been formed. Nitric acid is then added, the solution precipitated with silver nitrate, and the estimation finished in the usual way. The precipitate may easily be washed from the flask on to the filter.

The following are some of the results obtained by the above method:—

Substance.	Boiling point.	Found.	Calculated.
Ethyl bromide	39°	73·28	73·4
„ iodide	71	81·36	81·41
„ „	„	81·5	81·41
Carbon tetrachloride	77	92·25	92·2
Ethylene chloride.....	82	71·46	71·7
„ „	„	71·4	71·7
Amyl chloride	100	33·29	33·33
Ethylene bromide.....	131	85·17	85·1
„ chloriodide	141	85·2	85·3
Acetylene bromiodide	150	88·78	88·8

Three analyses of an impure specimen of benzal chloride yielded, 43·3, 43·6, 43·3 per cent. chlorine; a determination by Carius' method gave 43·6 per cent. The above experiments, made with compounds of very various composition and boiling points, will suffice to show that the method described is capable of yielding accurate results. The time occupied by a complete estimation is about two and a half hours.

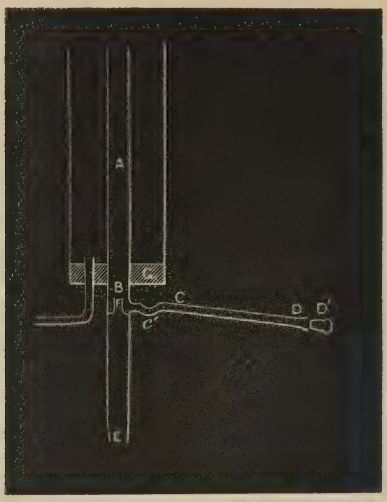
The experiments here described were made in the Laboratory of University College, London.

XVI.—*A Modified Liebig's Condenser.*

By W. A. Shenstone, Lecturer on Chemistry at Clifton College.

For effective working the original form of Liebig's condenser leaves nothing to be desired. It has, however, the disadvantage of occupying a great deal of space, and when used as part of an arrangement for digesting substances which are subsequently to be distilled, as in the preparation of formic acid by heating oxalic acid with glycerol, or in the preparation of ethyl iodide by digesting together red phosphorus, alcohol and iodine, there is a certain amount of trouble and loss of time in arranging it for distilling after the digestion is completed. These disadvantages, and especially the former, as I frequently want to have several operations in which condensers are employed simultaneously on a small lecture table, led me to try the modification I now describe. It is, as I expected, superior to the original form in taking

up but little space, and in its ready adaptability to the purposes of digesting and distilling without rearrangement; and the only objection I find to it is that, as the distillate is delivered rather near to the source of heat, it would be somewhat dangerous to employ it in distilling highly volatile and inflammable substances such as ether and benzene.



A tube A, which may be of any convenient size, is fitted in the ordinary way inside a larger glass tube, for which purpose I think the old-fashioned method of employing corks answers better than the modern plan, in which the outer tube is contracted at its ends and connected with the smaller tube by pieces of india-rubber tube. At B the tube A has a small projecting tube F, about 10 mm. in length. Into the side of A, so as to be below the level of the open end of F, a side tube C, having a slight dip at c', is joined on, its open end D being about 5 mm. below the level of the other end. A small stopper is ground into C at D. D may conveniently be 2 mm. to 3 mm. in diameter.

The end E can be attached to flasks by means of corks, or as might occasionally be desirable, can be ground to fit the neck of a flask.

When the condenser is in action, the vapour passes up through F, is condensed in A, and falls into the annular space around F at B. If the stopper is fixed at D, this space soon fills, and then, as further condensation occurs, the products overflow into the flask through F. The amount that collects at B with a well-made tube is very small, as the

air in C usually prevents the liquid from flowing into it when the stopper is fixed. When the apparatus is to be used for distilling, the stopper D′ is removed, and the distillate then flows out at D. The bend at *c′* was made in order that the first portions condensed might flow there, and so prevent any vapour from escaping by C at the early part of the operation; from what I see of the action of the tube, I think, however, that it is not necessary.

The outer tube should be brought down as near to the joint as possible: for the vapour coming up through F slightly warms the liquid at B, so that it is delivered at a slightly higher temperature than that of the water in the condensing jacket, and it is desirable to avoid this as far as possible.

When the temperature of the vapour must be known, I hang a thermometer inside E by means of a little hook of platinum wire. The length of the tube therefore from B to E should be such that there shall be room for an ordinary thermometer between the point B and the level of the liquid in the flask below. It is perhaps an advantage that in thus using this condenser, the actual temperature of the vapour is observed, as the stem of the thermometer is entirely immersed in it.

Mr. Cetti, the maker of the tube from which this is drawn, tells me that for fractional distillation, if, as might be the case, the form of tube proposed by Dr. Armstrong were employed, there would be no difficulty in grinding the end E to fit the upper end of the fractionating tube.

I have found this form of condenser so compact for moving about, and so easy and convenient to work with, especially for lecture purposes, that, as I believe such a modification has not been described before, I have thought it might be worth while to bring it under the notice of the Society.

XVII.—*On Some Fluorine Compounds of Uranium.*

By Arthur Smithells, B.Sc. (Dalton Scholar in the Laboratory of The Owens College).

I. Since the preparation of uranium oxyfluoride by Berzelius, the fluorine compounds of uranium have been investigated by Carrington Bolton (*Zeitschr. f. Chem.* [2], **353**; *Bull. Soc. Chim.*, 1866, **2**, 450) and more recently by Ditte (*Compt. rend.*, **91**, 115). As the results obtained by these two chemists do not agree, the present experiments

were undertaken at the suggestion of Professor Roscoe, in order to clear up the question.

The starting point in both the above cited researches was green uranoso-uranic oxide, U_3O_8. By the action of aqueous hydrofluoric acid on this body a voluminous green powder and a clear bright yellow solution are produced. The green powder, according to Bolton, is uranous fluoride, UF_4, whilst the yellow solution upon evaporation gives an almost white amorphous mass, possessing the physical properties of a body obtained by Berzelius (*Lehrb. d. Chem.*, **3**, 1099) by the action of hydrofluoric acid on uranic hydrate, and to which he assigned the formula UO_2F_2. The equation representing the action of hydrofluoric acid on the green oxide would therefore be :—

$$UO_2,2UO_3 + 8HF = UF_4 + 2UO_2F_2 + 4H_2O.$$

Ditte on the other hand assigns to the green powder the formula UO_2F_2, with the name *uranyl fluoride*. His description of the physical and chemical properties of the substance agrees with that of Bolton, but in addition he noticed a decomposition on heating in a closed crucible, viz., the formation of a white crystalline sublimate. With regard to the yellow solution, Ditte states that it is essentially a solution of uranium hexfluoride, and that on evaporation transparent yellow crystals are deposited, which when dried at 100° C. have the formula UF_6,8HF. From these crystals he obtains the pure hexfluoride by calcining in a crucible until partial decomposition ensues, then extracting with water, and crystallising the UF_6. The equation representing the action of hydrofluoric acid on the green oxide is given by him as follows :—

$$U_3O_8 + 18HF = 2(UF_6,2HF) + UO_2F_2 + 6H_2O + H_2.$$

He states that this may be verified by heating a known weight of U_3O_8 with hydrofluoric acid and weighing the resulting compounds, and that the rationale of the reaction is the splitting up of the U_3O_8 into UO_2 and UO_3; the former, acting as a simple body unites with the fluorine of the hydrofluoric acid, setting hydrogen free. The UO_3 gives an acid hexfluoride and water.

Action of Hydrofluoric Acid on the Green Oxide, U_3O_8.

That the above equation given by Ditte is unlikely to express the reaction, may be argued from the fact that the liberation of hydrogen from an acid by the action of a metallic oxide is contrary to all experience. And again, the confirmation by weighing the products from a known weight of the green oxide will not hold good, for as will afterwards be evident, the only one capable of being weighed with

accuracy is the green powder. If Bolton's formula be correct, one molecule of U_3O_8 (= 848) gives one molecule of UF_4 (310), and by Ditte's equation one molecule of U_3O_8 (= 848) gives one molecule of UO_2F_2 (= 316). The difference here, which amounts to about 0·7 per cent., is evidently too small to render the operation a means of verifying either theory, even if it could be conducted accurately.

The question as to the evolution of hydrogen in the reaction was decided experimentally by treating 100 grams of the green oxide in a leaden retort with aqueous hydrofluoric acid, and collecting the evolved gases (if any) over a pneumatic trough. In Ditte's equation one molecule of U_3O_8 (848) gives one molecule of hydrogen, so that 100 grams should yield $\frac{22{\cdot}3 \times 100}{848} = 2{\cdot}6$ litres of hydrogen. In my experiment considerable heat was evolved by the chemical action, and rather less than a quarter of a litre of gas passed into the collecting cylinder. This on examination proved to be air expanded from the hot retort. In order to confirm the conclusion that no hydrogen is liberated during the reaction, the experiment was repeated, the delivery-tube of the retort being carried to the top of the receiving cylinder, and after the air had been expelled into the latter as before, the apparatus was allowed to cool *in situ*. The result was that only an inappreciable quantity of air was left in the cylinder. It is true that effervescence is sometimes noticeable when the green oxide is treated with hydrofluoric acid; but this is due to the heat of chemical action expelling the air which is entangled in the fine powder, and is not observable if the action proceeds slowly.

Uranous Fluoride, UF_4.

After the reaction just described, the retort contained the green powder and yellow solution. The two were separated, and the powder washed with distilled water—a very tedious process, as the substance either passes through the pores of the filter-paper or fills them up. After washing for a few days in this manner, the green powder was usually transferred to a large beaker and washed for a long time by decantation. The difficulty of getting rid of the last traces of hydrofluoric acid is very great. When this had been accomplished as nearly as possible, the substance was dried at 100° until no further loss of weight ensued.

In the analyses to be quoted, the uranium was usually determined by means of ammonium sulphide, the mixed sulphur and uranous oxide being very strongly ignited and weighed as U_2O_5. This process gave most satisfactory results when all the precautions mentioned by Remelé (*Zeits. Anal. Chem.*, **4**, 379) and Zimmerman

(*Annalen Chem.*, **204**, 204) were observed. Sometimes in the case of a soluble fluoride, the uranium was determined by evaporating with sulphuric acid, adding excess of ammonium carbonate, again evaporating, and finally igniting to the oxide. In all determinations the uranium was weighed as U_2O_5, which being the final product of the application of intense heat to the other oxides, can easily be obtained pure. Fluorine was in all cases determined as calcium fluoride in the usual way. The total hydrogen (existing as water or in acid combination) was estimated by heating with anhydrous sodium carbonate and weighing the water absorbed by a calcium chloride tube (Bunsen).

The green powder was fused with sodium carbonate and the constituents determined with the following results:—

0·8645 gram	gave	0·7450 gram	U_2O_5	= 73·87	Mean = 74·03
1·2240 „	„	1·0595 „	„	= 74·19	per cent. U.
0·5440 „	„	0·2785 „	CaF_2	= 24·94	Mean = 25·73
0·5480 „	„	0·2985 „	„	= 26·53	per cent. F.

The results comparatively stated are as follows:—

		Calculated.	
	Found.	UF_4 (Bolton).	UO_2F_2 (Ditte).
U	74·03	75·95	77·42
O	—	—	10·32
F	25·73	24·05	12·26
	99·76	100·00	100·00

This shows that the green powder in question is uranous fluoride, UF_4, and not UO_2F_2, the difference between the found and calculated proportions being mainly due to the presence of free hydrofluoric acid.

Uranous fluoride is—as described by Bolton—insoluble in water, hardly attacked by weak acids, and is only with difficulty dissolved by concentrated acids. Heated on platinum-foil it loses fluorine, and, without melting, gives U_3O_8.

α-Uranium Oxyfluoride.—The most remarkable property of uranous fluoride is one described by Ditte as pertaining to UO_2F_2, viz., the formation of a white crystalline "sublimate" on heating the substance in a closed crucible. The crystalline mass is very bulky, but extremely light, and it usually contains a quantity of very minute crystals of UO_2. The quantity obtained depends on the manner in which the crucible containing UF_4 is heated, and when a certain amount has been obtained, it cannot be increased by continued heating,

but begins to decompose. If, however, at this point the crucible be allowed to cool, the crop of crystals removed, and the heating renewed, a further quantity of crystals can be obtained, and in this way as many as five crops have been yielded. It is evident from these facts that a certain amount of oxygen is necessary for the process, whilst an excess causes a different decomposition, viz., the conversion of UF_4 into U_3O_8.

The preparation of this white crystalline compound in quantity presents great difficulties; the fact of its being prepared from a fused fluoride forbidding the use of any but platinum apparatus, and, as just pointed out, only a limited amount of oxygen must be present.

No more successful method was found than that of heating about 1 gram of uranous fluoride in a platinum crucible of the ordinary size, raising the temperature as quickly as possible, and leaving the mass to cool at the end of five minutes.

After the fourth application, the fluoride acquires the appearance of green sealing-wax, and begins to yield crops of crystals. The final residue in the crucible seems to consist chiefly of UO_2. Many repetitions of the above process are necessary in order to obtain a sufficient quantity of the substance for analysis, and, as it is very hygroscopic, it is first necessary to estimate the amount of water present by heating with anhydrous sodium carbonate as previously described. When freshly prepared the substance is anhydrous.

The following is the result of an analysis:—

0·167 gram gave 0·0137 gram H_2O; 0·51 gram gave 0·4235 gram U_2O_5 and 0·1122 gram CaF_2. This corresponds to the composition UO_2F_2 for the anhydrous body.

Ditte assigned to it the formula UOF_4, and gave the following equation of formation, which he verifies by weighing the products from a known weight of the green powder:—$2UO_2F_2 = UOF_4 + UO_2 + O$. As the green powder has been shown to be UF_4, the equation cannot hold good.

The following is a comparison of results:—

		Calculated.	
	Found.	UO_2F_2.	UOF_4 (Ditte).
U.....	77·57	77·42	72·29
O.....	10·74 (diff.)	10·32	4·82
F.....	11·69	12·26	22·89
	100·00	100·00	100·00

α-Uranium oxyfluoride is exceedingly soluble in water, giving a yellow solution. Heated in air it is gradually converted into the green oxide. An attempt to volatilise it in a current of carbon

dioxide failed, the body only undergoing a slight change when heated above its temperature of formation. If a considerable quantity of a solution of the normal and acid fluoride of potassium be added to a solution of α-uranium oxyfluoride, and the mixture gently evaporated, well-defined yellow crystals of quadratic potassium fluoxyuranate, $UO_2F_2,3KF$, are deposited. The crystallography of this latter compound has been carefully studied by Baker (*Chem. Soc. J.*, Nov., 1879), and I have, fortunately, had his evidence as to the identity of the salts.

β-Uranium Oxyfluoride, UO_2F_2.—The yellow solution formed in addition to uranous fluoride by the action of hydrofluoric acid on the green oxide was heated to expel excess of acid and allowed to evaporate. A pale-yellow saponaceous mass remained. Evaporated under different circumstances in air, by heat, or *in vacuo* over sulphuric acid and lime, in one case only was there a deposit obtained which could be called even semi-crystalline. In this case there were formed scales of a nacreous lustre resembling cadmium bromide. The semi-crystalline mass was dried at 100° C. and analysed with the following results:—

0·3200 gram	gave	0·3000 gram	U_2O_5	= 80·34	79·91 per cent. U.
0·8185 „	„	0·7590 „	„	= 79·49	
0·3670 „	„	0·0734 „	CaF_2	= 9·75	10·17 per cent. F.
0·4035 „	„	0·0875 „	„	= 10·59	

The following is a comparison of results with those of previous observers:—

		Calculated.	
	Found.	UO_2F_2 (Bolton).	UF_6,8HF (Ditte).
U....	79·91	77·42	46·59
O....	9·87 (diff.)	10·32	—
F....	10·71	12·26	51·85
H....	trace	—	1·56
	100·00	100·00	100·00

Bolton did not analyse the substance.

These results, whilst disagreeing entirely with those of Ditte, do not exactly correspond with the composition UO_2F_2, probably because on heating for some time at 100° the body loses fluorine—a process which continues as the temperature is raised until the whole is converted into U_3O_8.

Another portion of the yellow solution was evaporated over sulphuric acid and lime until the weight remained constant. The residue was analysed with the following results:—

0·8495 gram gave	0·6899 gram	U_2O_5	= 69·60	}	69·36 per cent. U.
0·7315 „ „	0·5899 „	„	= 69·12	}	
1·2885 „ „	0·3264 „	CaF_2	= 12·34	}	12·46 per cent. F.
1·3340 „ „	0·3450 „	„	= 12·59	}	
0·6170 „ „	0·0720 „	H_2O	= 1·28	}	1·29 per cent. H.
0·7760 „ „	0·0890 „	„	= 1·29	}	

If the difference be regarded as oxygen the above analysis corresponds fairly well with a molecular formula UO_2F_2,HF,H_2O. Calculating the uranium as oxyfluoride and the excess of fluorine as hydrofluoric acid, and the remainder of the hydrogen as water, we obtain the following :—

UO_2F_2.....	89·59
HF	1·56
H_2O.....	10·89

This result, although from the nature of the case only approximate, is, when taken in conjunction with the previous analysis of a dried specimen of the compound, sufficient to show that the yellow liquid obtained on treating U_3O_8 with hydrofluoric acid, consists of a solution of oxyfluoride of uranium, UO_2F_2.

Heated on platinum-foil, βUO_2F_2 gives U_3O_8; in a closed crucible it undergoes decomposition more slowly, giving the dioxide. It is extremely soluble in water and alcohol, and gives potassium fluoxyuranate when its solution is evaporated with a mixture of normal and acid potassium fluorides.

It is evident therefore that the solutions of α- and β-oxyfluorides possess the same properties, and it is important to note the analogy presented here by uranium with another member of the group to which it has been finally relegated. Molybdenum oxychloride also exists in two isomeric forms, α and β, the former of which can be prepared by heating the chloride in air, an operation analogous to the preparation of α-uranium oxyfluoride from uranous fluoride.

II. *The Fluorine Compounds of Uranium with the Alkalis.*

In a further paper (*Compt. rend.*, **91**, 166) Ditte describes new fluorine compounds of uranium and the alkalis. The salts previously known comprised two classes, the uranofluorides and the fluoxyuranates. The former were discovered by Bolton (*Zeitsch. f. Chem.*, N.S. [2], 353), and included two with the formulæ UF_4,KF and UF_4,NaF. The formation of the fluoxyuranates was first described by Berzelius (*Lehrb. d. Chem.* [iii], 1099, 1845), and the compounds afterwards examined by Bolton (*loc. cit.*), who obtained the potassium,

sodium, and ammonium compounds. The fluoxyuranates were further investigated by Baker (*Chem. Soc. J.*, Nov. 1879), who showed that the potassium salt exists in three modifications, $UO_2F_2,3KF$, $2UO_2F_2,5KF$, and $2UO_2F_2,3KF,2H_2O$, crystallising respectively in the quadratic, triclinic, and monoclinic systems.

The Series $UO_2F_2.4MF$ *of Ditte.*—By fusing the green uranoso-uranic oxide, U_3O_8, with an alkaline fluoride, Ditte claims to have prepared a series of insoluble crystalline salts of the general formula $UO_2F_2,4MF$. The methods of preparation described by him have been followed in every particular, and compounds have been obtained which correspond in appearance with his descriptions. By adding U_3O_8 to fused potassium fluoride rendered feebly alkaline by the addition of potassium carbonate, and heating over the blowpipe for a short time, a yellow mass is obtained, which on lixiviation with water leaves undissolved transparent golden-yellow crystalline plates. These are insoluble in hot or cold water, but are readily dissolved by dilute acids. They are unaltered by heating in air, but when heated in a current of hydrogen, they acquire a greenish-black colour without altering their form. The crystals consist of thin plates, often with hexagonal outlines, and belong to the rhombic system. They are feebly dichroic, and exhibit a banded twin structure, which becomes very distinct in polarised light. The bands run in three systems parallel to the sides of the hexagon, and in addition there is a series of less regular markings at right angles to one edge. The two optic axes are visible in the polariscope, and their plane is apparently perpendicular to that of the plate.

The sodium salt is prepared in a precisely similar manner, and has a similar appearance, except that the crystals are smaller and have a deep orange colour. An attempt to prepare the lithium salt has not yet proved successful.

Although these salts correspond exactly in appearance with those described by Ditte as $UO_2F_2,4KF$ and $UO_2F_2,4NaF$, when an attempt was made to estimate the fluorine, only 0·1 or 0·2 per cent. was found. And indeed specimens have been prepared in which no trace of fluorine could be detected, the presence of this element apparently arising from imperfect washing, which with the sodium salt is very liable to be the case, owing to the sparing solubility of sodium fluoride.

These compounds present many points of similarity to the crystalline uranates described by Zimmermann (*Ber.*, **14**, 440), and their composition, so far as it has been determined, approaches to that of the diuranates, or still more closely to that of the intermediate products obtained by Zimmermann in the preparation of those bodies. Further experiments on the formation and composition of the potas-

sium uranium compounds are necessary, however, before coming to a definite conclusion.

The Series $UOF_4,4MF,xH_2O$ *of Ditte.*—If instead of using the normal fluoride of potassium, a mixture of U_3O_8 and the acid fluoride KF,HF be fused, different results are obtained. If, as soon as the mass is just fused, it be allowed to cool, it appears of a bright green colour, and on treatment with water gives a yellow solution, and an insoluble green powder resembling uranous fluoride. If, however, the fusion of the mass be continued, the green colour is gradually changed to a pale yellow, and at this stage treatment with water effects almost complete solution. On still further heating, the colour becomes tinged with orange, until finally, after prolonged fusion, the crucible contains the crystalline compound which has just been described as resulting from the action of U_3O_8 on fused normal fluoride of potassium. An explanation of these changes will be offered immediately.

The yellow solutions obtained by lixiviating the fused masses, freed from insoluble substances by filtration, were left at rest after being slightly concentrated, or were evaporated on a water-bath. In both cases small but very well-defined transparent crystals were obtained. Under the microscope these were at once recognised as quadratic potassium fluoxyuranate, and analysis gave confirmatory results:—

1·1755	grams	gave	0·6898	gram	U_2O_5	= 50·29	per cent. U.
1·1755	„	„	0·6255	„	K_2SO_4	= 23·90	„ K.
0·6720	„	„	0·2648	„	CaF_2	= 19·20	„ F.

	Found.			Calculated.
	a.	*b.*	*c.*	$UO_2F_2,3KF$.
U	50·29	49·86	49·96	49·56
K	23·90	—	—	24·24
F	19·20	18·75	—	19·58
O	—	—	—	—

(*b*) and (*c*) are partial analyses of other specimens of the salt.

It appears therefore that when acid potassium fluoride and green uranoso-uranic oxide are fused together, the hydrofluoric acid of the acid salt is liberated, and acts on the oxide as shown in the first part of this paper, producing uranous fluoride, UF_4, and β-uranium oxyfluoride, UO_2F_2. In the early stages of the fusion, the former seems to unite with potassium fluoride to form the double salt UF_4,KF, whilst one molecule of UO_2F_2 and three of KF form the fluoxyuranate. By further heating, the uranofluoride is converted into the fluoxyuranate, whilst the result of prolonged fusion of the latter is the

insoluble crystalline compound, which is also obtained by using the normal instead of the acid potassium salt, and which contains no fluorine. This last change was noticed by Bolton (*loc. cit.*).

According to Ditte, the soluble yellow crystals obtained in the above operation have the formula $2(UOF_4,4KF)3H_2O$ or $UOF_4,4KF,3H_2O$, according to the temperature at which they are deposited, whereas my results show that they are the fluoxyuranate of potassium, $UO_2F_2,3KF$, already known. Moreover, Ditte adds that by adding caustic potash to the yellow solution obtained by treating U_3O_8 with hydrofluoric acid, the same bodies are produced, and that by dissolving them in water containing acid potassium fluoride, and recrystallising at a temperature of from 50—60°, a compound is obtained with the formula $UOF_4,4KF,H_2O$. This is opposed to the results obtained by Berzelius and Bolton, and to those detailed in the first part of this paper, for the yellow solution obtained by acting on U_3O_8 with hydrofluoric acid has been shown to contain uranium oxyfluoride. In addition it contains the excess of hydrofluoric acid employed, which would give potassium fluoride on treating the solution with caustic potash, and so lead to the formation of the salt $UO_2F_2,3KF$. When this salt is dissolved in water containing not more than 13 per cent. of acid fluoride of potassium the triclinic fluoxyuranate, $2UO_2F_2,5KF$, crystallises out (Baker, *loc. cit.*).

In no case have I obtained a salt corresponding in composition with either of the three formulæ given by Ditte, and it appears that the compounds obtained by him were in reality only the three fluoxyuranates already known.

Postscript.

In a recently published paper (*Compt. rend.*, **95**, 988), Ditte describes the "Preparation of some Crystallised Uranates in the Dry Way" by fusing a mixture of the alkaline (or alkaline-earth) chloride with green uranoso-uranic oxide, U_3O_8. No reference is made in the paper to the work done on this subject by Zimmermann (*Ber.*, **14**, 440; *Annalen*, **213**, 290), who, following practically the same process, obtained widely different results. The latter chemist has shown that by fusing potassium or sodium chloride with U_3O_8, crystalline diuranates ($M_2O,2UO_3$) are obtained, but that lithium chloride under similar circumstances gives a normal lithium uranate, Li_2O,UO_3. For an account of the precautions which were taken by Zimmermann in the study of these compounds, reference must be had to the original paper, where the modes of preparation and analysis are described in detail. Ditte, however, gives no analytical results in support of the correctness of his observations.

It is also to be remarked that in an earlier paper (*Compt. rend.*, **91**, 166) previously referred to, Ditte claims to have obtained compounds which he formulates as double fluorides of uranium and the alkalis, by fusing alkaline fluorides with U_3O_8. In repeating these experiments I have succeeded only in obtaining bodies which approach the diuranates of Zimmermann in composition and properties. That such is likely to be the case might be inferred from the experiments of Zimmermann, and now of Ditte himself, since both prepare uranates or diuranates by fusing U_3O_8 with the haloïd salts of the alkalis.

XVIII.—*On the Volume Alteration attending the Mixture of Salt Solutions.*

By W. W. J. Nicol, M.A., B.Sc., F.R.S.E., Lecturer on Chemistry, Mason College, Birmingham.

The value of a more exact and extended knowledge of the volume alteration attending the mixture of salt solutions, as a means of extending our knowledge of the nature of solution, has not been fully recognised; so far as I am aware, the only experiments in this direction are those of Kremers (*Pogg. Ann.*, **96**, 103), and MM. Favre et Valson (*Compt. rend.*, **74**). With the view of indicating some errors into which the last-named observers have fallen, and of inducing others to enter this field of research, I venture to lay this paper before the Society.

My experiments were made incidentally while I was gathering data for a paper on the "Nature of Solution"; but they show a most complete agreement among themselves, and correspond with the thermal results obtained by Berthelot. The solutions I experimented with were molecular ones, that is, they contained one, two, three, or more molecules of salt dissolved in 100 mols. of water. These, after determination of specific gravity, were mixed in equal volumes by weighing out 10 times the specific gravity in grams; in no case does the error exceed $\pm$ 0·0003 c.c. in volume or $\pm$ 0·00002 in the specific gravity.

My experiments naturally fall under the three heads—

(*a.*) Mixture of solutions containing the same metal or the same salt radical (no double decomposition possible).

(*b.*) Mixture of solutions containing different metals and salt radicals (double decomposition possible).

(*c.*) Cases where double salts may be formed.

(a.) *No Double Decomposition Possible.*

Table I. Mixture of NaCl and KCl, various strengths, and in various proportions. The strength of the solution is expressed in terms of molecules of salt to 100 mols. of water.

Table I.

Strength.	Sp. gr.	Sp. gr. of mixture.	Mean sp. gr.	C.
NaCl	1·02238	1·02394	1·02390	3·4
KCl	1·02542			
5NaCl	1·00277	1·10875	1·10864	9·8
5KCl	1·11450			
5NaCl	1·10277	1·06363	1·06258	99·0
NaCl	2·02238			
5KCl	1·11450	1·07089	1·06996	87·0
KCl	1·02542			
5NaCl	1·10277	1·96503	1·06405	92·0
KCl	1·02542			
5KCl	1·11450	1·06946	1·06844	96·0
NaCl	1·02238			

C = contraction. Volume before mixing = 100·000.

Again, dilution of the above solutions with an equal volume of water gave the following results :—

Table II.

Salt.	Sp. gr.	Sp. gr. after dilution.	Mean sp. gr.	C.
NaCl	1·02252*	1·01142	1·01126	15·8
KCl	1·02542	1·01283	1·01271	12·0
5NaCl	1·10281*	1·05295	1·05142	144·5
5KCl	1·11449	1·05868	1·05725	135·0

Now the mixture of NaCl and KCl should give a contraction equal to the difference in contraction on dilution of NaCl and KCl separately, and the same should be true of 5NaCl and 5KCl. The actual numbers are :—

* The specific gravity of the solutions was redetermined before dilution; the slight differences are due to evaporation.

Strengths.	Difference in contraction on dilution.	Contraction on mixing.
NaCl and KCl	3·8	3·4
5NaCl and 5KCl	9·5	9·8

Further, the contraction observed on mixing salt solutions of different strengths is the difference between the contraction produced by the dilution of the strong one down to the mean strength and the expansion due to the concentration of the weak solution up to the mean. This may be expressed as follows:—

C − E = observed contraction, and in the four cases in Table I—

$$\begin{aligned} C_{Na} - E_{Na} &= 99, \text{ and} \\ C_{K} - E_{K} &= 87 \\ \hline & 186, \text{ and} \end{aligned}$$

$$\begin{aligned} C_{Na} - E_{K} &= 92, \text{ and} \\ C_{K} - E_{Na} &= 96 \\ \hline & 188 \end{aligned}$$

These two sums should be equal, and such is practically the case.

(b.) *Double Decomposition Possible.*

Table III contains the results obtained by mixing 5NaCl and $5KNO_3$; and the converse, 5KCl and $5NaNO_3$. The experiment was made in each case at 20° C. and 40° C.

TABLE III.

t.	Salt.	Sp. gr.	Sp. gr. of mixture.	Mean sp. gr.	C.
20°	$5KNO_3$	1·14880	1·12577	1·12578	− 1
	5NaCl	1·10276			
40°	$5KNO_3$	1·14518	1·12276	1·2268	7 +
	5NaCl	1·10018			
20°	$5NaNO_3$	1·13810	1·12664	1·12632	29
	5KCl.....	1·11454			
40°	$5NaNO_3$	1·13362	1·12359	1·12315	38
	5KCl.....	1·11268			

There is no doubt whatever that in the second case double decom-

position has taken place, for the differences between the sets of numbers are the same—

t.	$5NaCl + 5KNO_3$.	$5KCl + 5NaNO_3$.
40°	C = 7 +	38 −
20	C = − 1	29
	Difference 8 +	9 −

within very narrow limits.

(c.) *A Double Salt Possible.*

Table IV.

Salt.	Sp. gr.	Sp. gr. of mixture.	Mean sp. gr.	C.
$\frac{CuSO_4 5H_2O}{2}$	1·04286	1·04027	1·04019	7 +
$\frac{K_2SO_4}{2}$	1·03753			

I do not feel justified in drawing any conclusion from the above; nor is it of any use to make further experiments: for in most cases of the formation of double salts which can be studied by this method, water of crystallisation enters into the composition of one or both of the component salts, in a proportion different from that in the resulting double salt. Until then we are able to trace the amount of volume change due to the water of crystallisation, the question of the condition of double salts in solution cannot be settled in this way.

In all the above instances there has been a change of volume observed, small it is true, but exceeding the experimental error, except in the case of $5NaCl + 5KNO_3$.

Now Favre and Valson neglect this change of volume, and in spite of their experiments clearly showing it, insist on the general truth of the following statement:—

When a salt is dissolved in water in which another salt is already dissolved, provided both salts are formed by strong bases and acids, the heat of solution is practically the same as that in pure water (thermoneutrality of Hess), and the specific gravity of the solution is the mean of the specific gravities of the salt solutions separately. In other words the presence of another salt interferes neither with the thermal

nor with the density effects of solution. Thus they correlate thermal and density neutrality.

Thermo-neutrality is a term introduced by Hess (*Ann. Chim. Phys.*, 1842) 40 years ago, and accepted as a correct statement of facts until Berthelot's experiments cast doubt on its accuracy. Berthelot (*Mécanique Chimique*, **1**, 69) gives the following formula as expressing the thermal relations existing on the mixture of two salts capable of undergoing double decomposition:—

$$K_1 - K = (N - N_1) - (N' - N_1'),$$

where K = the heat disengaged on mixing the solutions of two salts such as AB and CD, K_1 = that evolved on mixing the reciprocal couple AD and BC. N and N_1 the heat of neutralisation of the two bases by one of the acids, N' and N_1', the corresponding quantities for the other acid. When the bases and acids are strong, then the quantities, K and K_1, and consequently their difference, are very small; thus Hess believed it possible to neglect them and to establish the principle of thermo-neutrality; but it is never rigorously true, and even if it be approximately so of salts of strong acids and strong bases, it fails to hold in other cases.

Favre and Valson disregard these slight variations of temperature on which Berthelot lays stress, and hold that when the acids and bases are both strong, true thermo-neutrality and density-neutrality exist. The data on which this last conclusion is based are as follows:—

TABLE V.

Salt.	Sp. gr.	Mean sp. gr.	Sp. gr. of mixture.	Δ.
$NaNO_3$	1·0540			
KCl.....	1·0444	1·0454	1·0445	0·0009
$\frac{(NH_4)_2SO_4}{2}$	1·0378			
$\frac{K_2SO_4}{2}$	1·0662	1·0720	1·0717	0·0003 –
$\frac{CuSO_4}{2}$	1·0777			

Strength = 1 equivalent in a litre.

They therefore disregard a difference of 0·0003 to 0·0009, and assume that these are due to experimental error, which is quite possible, as their determinations apparently were made with a bottle, and not with the more accurate Sprengel tubes; but as these numbers exceed greatly the density-change on dilution of such weak solutions

with water, they must of necessity be greater than those accompanying the mixture of salt solutions.

My experiments show that—

(1.) When two salt solutions, which cannot experience double decomposition, are mixed, a change of volume takes place, due to the different affinities of the salts for water.

(2.) That double decomposition takes place in solution, and that the volume-change is an index and even a measure of this.

I hope soon to be able to lay before the Society a more extended series of experiments on this subject.

XIX.—*Two New Aluminous Mineral Species, Evigtokite and Liskeardite.*

By Walter Flight, D.Sc., F.G.S., of the Department of Mineralogy, British Museum, South Kensington.

Evigtokite.

This mineral, described as "fluoride of aluminium," and obtained from the cryolite bed of Greenland, was bought in June, 1861, of Mr. Tayler; it came, together with eudialyte, arfvedsonite, columbite, black cryolite, fergusonite, sapphirine, garnet, allanite, &c., all from that locality. The whole mass consists of the same mineral, unaccompanied by any associated minerals; it is made up of a congeries of minute white transparent crystals, mostly broken up, and lying entangled amongst each other in every sort of direction, which gives the mass an appearance of opacity much resembling that of kaolin or chalk. The hardness is very low; particles are easily detached or broken in twain between the fingers.

When the mineral is heated in a glass tube, water is given off, and then hydrofluoric acid, with a strong acid reaction; the mineral does not melt. It was pounded and dried over sulphuric acid, and was found to have the following composition, when the loss in weight is taken to be water:—

					Equivalents.
Aluminium ..	16·23;	with fluorine	33·64 =	49·87 ..	0·59
Calcium	22·39;	,, ,,	21·27 =	43·66 ..	1·12
Sodium	0·43;	,, ,,	0·33 =	0·76	
				94·29	
Water				5·71 ..	0·63
				100·00	

These numbers, it will be seen, correspond closely with the formula—

$$Al_2F_6,2CaF_2 + 2H_2O.$$

The question suggests itself, may this body have been produced by the action of water containing lime sulphate on cryolite?

No mineral described in Dana's *A System of Mineralogy*, and its several appendices, or in the recent paper of Josef Brandl (*Annalen*, Band 213), on the composition of minerals of the cryolite group, corresponds with this mineral in composition, and I have therefore proposed to give it the name which stands at the head of this note.

Liskeardite.

To Mr. Richard Talling, of Lostwithiel, Cornwall, who has added so many new British species to the collection, belongs the honour of having noticed this mineral in 1874. At a later date, in 1877, some further specimens were sent to the British Museum, by Mr. Barnett, of Chyandour, near Penzance. It is a white crystalline mineral, with a slight tint of blue or greenish-blue, and occurs as a layer, sometimes a quarter of an inch thick, generally of a uniform fibrous structure, lining hollows or encasing quartz and other minerals. It is associated with earthy chlorite and quartz, iron pyrites, some copper pyrites and mispickel being disseminated in the lode material. Scorodite, in boss-like aggregations also occurs with it, and in at least one instance the interior of the bosses of scorodite is filled with the mineral in question.

An analysis of this mineral, made in 1878, showed it to have the following composition:—

Ferric oxide	7·640		
Alumina	28·229		
Arsenic oxide	26·962		
Sulphuric oxide	1·111		
Copper oxide	1·027		
Lime	0·719		
Water at ordinary temp.	4·351		
„ 100°	10·962	(six equivalents)	34·053
„ 120°	5·551	(three equivalents)	
„ 140—190°	8·220	(seven equivalents)	
„ with lead oxide	4·969		
	99·741		

These numbers correspond with the formula—

$$R'''AsO_4,8H_2O,$$

when R represents aluminium, with a notable quantity of iron. The tint of the mineral seems to be due to the presence of about 1 per cent. of copper oxide, and a small amount of a sulphate is also present. The presence of the sulphate and the general character of the composition would lead one to place the mineral with pitticite, or "eisensinter," but the formula is so nearly that of an arsenical, instead of a phosphatic evansite, that the true place of the mineral seems to be near the evansite of the late Mr. D. Forbes.

It seemed desirable to redetermine the amount of water which left the mineral at the several temperatures: this was done with great care, and with the following results:—

It lost in a vacuum, over sulphuric acid, at ordinary temperatures, 4·722 per cent., or *four* atoms of water.

It lost, at 100°, altogether 11·266 per cent., which is about *eight* atoms of water.

It lost between 100° and 120° altogether 4·392 per cent., or *four* atoms of water.

It lost between 120° and 144° altogether 3·435 per cent., or *three* atoms of water.

It lost between 145° and 160° altogether 2·448 per cent., or *two* atoms of water.

It lost between 160° and 190°, altogether 2·351 per cent., or *two* atoms of water.

The mineral was then heated with an excess of pure lead oxide in a current of dry air, and the water collected in a calcium chloride tube. The number obtained was a further loss of 4·896 per cent., or *four* more atoms of water.

XX.—*On the Absorption of Weak Reagents by Cotton, Silk, and Wool.*

By Edmund J. Mills, D.Sc., F.R.S., and Jokichi Takamine, of the Imperial College of Engineering, Tokio, Japan.

Cotton, silk, and wool are definite chemical substances, whose composition is represented by the formulæ $C_6H_{10}O_5$, $C_{24}H_{38}N_8O_8$, and $C_{42}H_{157}N_5SO_{15}$* respectively. It has long been known that they are capable of absorbing from weak aqueous solutions the ordinary acid and alkaline reagents.

* This expression has been calculated by ourselves from the summary of analyses in *Gmelin's Handbook*, **18**, 351.

The object of the following research is first the quantitative measurement of such absorption, under conditions to be subsequently indicated; and then to ascertain whether the absorption is amenable to laws already established in other fields of chemical investigation.

Our work has naturally fallen into two divisions, viz., (I), the rate and amount of absorption of individual reagents; and (II), the ratio of absorption of mixed reagents.

Part I.

A number of tall cylindrical wide-mouthed stoppered bottles, holding about 300 c.c. (12 cm. × π[3 cm.]^2), were filled each with 250 c.c. of an acid or alkaline solution of known strength, and kept at a constant temperature during experiment by immersion in a current of water from the main; equal weights of the tissue (in nearly every case 3 grams) were placed in each of these bottles, and the time noted. After a suitable interval, the tissue was removed from the bottles by means of glass rods. A known volume of the liquid in the bottle from which the tissue had been removed was now taken and tested volumetrically for residual acid or alkali, phenolphthaleïn being the indicator. The diminution of strength gives the amount of absorption. Such determinations having been made with a series of bottles, each of which contained the tissue for a different length of time, the differences in amount of absorption in different bottles enable us to infer the rate of and total absorption.

The wool employed was fine Cashmere wool; the silk, a plain pure silk, freed from Prussian blue; the cotton, a pure calico;—all in the piece. These were all previously washed with very weak sodic hydrate, water, very weak hydric chloride, and distilled water successively in the cold. The acids and alkali we employed were hydric sulphate, hydric chloride, and sodic hydrate.

The following table comprises the results of a trial series of experiments:—

Table I.

Material.	Weight of the material.	Time in weeks.	Acid.	Total absorption.	Acids per c.c.	Mean temperature.
Silk	1 gram	1	Hydric sulphate	0·002863	0·00004833	16·7°
,, ...	,,	2	,, ,,	0·003063	,,	16·3
,, ...	,,	2	Hydric chloride	0·000805	0·0000180	16·0
,, ...	,,	2	Hydric tartrate	0·001897	0·0001479	16·0
Wool ..	,,	1	Hydric sulphate	0·004552	0·00004833	16·7
,, ..	,,	2	,, ,,	0·004736	,,	16·3
,, ..	,,	2	Hydric chloride	0·001225	0·0000180	16·0
,, ..	,,	2	Hydric tartrate	0·004715	0·0001479	16·0

The silk employed in the above experiments contained 6·8 per cent. of moisture and an inappreciable amount of ash. The results show clearly the points intended to be ascertained, viz. (1) that wool and silk do really absorb the acids in question, and (2) that the greater part of the effect is completed, at the ordinary temperature, in a week's time.

Henceforward the following points are common to all tables:— (1) Unit of time $\frac{1}{4}$ hour; (2) volume of liquid in each bottle = 250 c.c.; (3) an equation, in which y stands for remaining absorbable reagent, and x the number of units of time.

TABLE IIa.—*Absorption of Hydric Sulphate by Wool.*

Hydric sulphate in each bottle = 0·187535 gram.

Weight of anhydrous wool 0·8728 gram (weighed hydrous with 12 per cent. of moisture: ash, 0·06 per cent.).

Equation, $y = 0{\cdot}01594(0{\cdot}77047)^x$.

Time.	Temp.	Sulphate absorbed.	Remaining sulphate.	Remaining sulphate calc.
0	—	—	—	0·01594
1	8·0°	0·00844	0·01350	0·01228
2	8 0	0·01087	0·01107	0·00946
3	8·0	0·01500	0·00694	0·00729
4	7·5	0·01594	0·00600	0·00562

Probable error of a single comparison, 0·00082 gram.

TABLE IIb.—*Absorption of Hydric Sulphate by Wool.*

Hydric sulphate in each bottle = 0·662575 gram.

Weight of anhydrous wool in each bottle 2·61 grams (weighed hydrous with 12·7 per cent. of water).

Ash in anhydrous wool 0·06 per cent.

Equation, $y = 0{\cdot}062614(0{\cdot}75432)^x$.

Time.	$t°$.	Sulphate absorbed.	Remaining sulphate.	Remaining sulphate calc.
—	—	—	0·06261	0·06261
1·93	4·0	0·025416	0·03720	0·03634
2	„	0·027000	0·03561	0·03563
3	„	0·037472	0·02514	0·02687
4	„	0·046131	0·01648	0·02027
6	„	0·052601	0·01001	0·01154
8	„	0·056258	0·00636	0·00656
12	„	0·058171	0·00444	0·00212
20	„	0·062165	0·00045	0·00022
28	„	0·062446	0·00019	0·00002
106	4·5	0·062614	—	—

Probable error of a single comparison, 0·00114 gram.

TABLE III.—*Absorption of Hydric Chloride by Wool.*

Hydric chloride in each bottle = 0·41810 gram.

Weight of anhydrous wool in each bottle 2·61 grams (weighed 3 grams hydrous with 12·7 per cent. of water).

Ash per cent., 0·05 per cent. in anhydrous wool.

Equation, $y = 0{\cdot}038702(0{\cdot}47217)^x + 0{\cdot}0028703(0{\cdot}93949)^x$.

$t°$ C. corr.	Time.	Chloride absorbed.	Remaining chloride.	Remaining chloride calc.
—	—	—	0·04157	0·04157
4·0	1·93	0·026900	0·01467	0·01164
„	2	0·030568	0·01100	0·01116
„	3	0·035051	0·00652	0·00645
„	4	0·038312	0·00326	0·00416
„	6	0·039208	0·00236	0·00240
„	8	0·039738	0·00173	0·00184
„	12	0·039942	0·00163	0·00136
„	20	0·040757	0·00082	0·00082
„	28	0·041165	0·00041	0·00050
4·5	106	0·041572	—	—

Probable error of a single comparison, 0·00076 gram.

TABLE IVa.—*Absorption of Sodic Hydrate by Wool.*

The reagent consisted of standard sodic hydrate diluted to the indicated strength.

Sodic hydrate in each bottle = 0·0765449 gram.

Weight of anhydrous wool in each bottle = 0·87288 gram (weighed hydrous with 12·72 per cent. of water and 0·06 per cent. of ash).

Equation, $y = 0{\cdot}013016(0{\cdot}58818)^x$.

Time.	$t°$ C.	Hydrate absorbed.	Remaining hydrate.	Remaining hydrate calc.
0	—	—	0·01302	0·01302
1	7·9	0·00620	0·00682	0·00766
2	8·0	0·00860	0·00441	0·00450
3	8·2	0·00918	0·00383	0·00265
4	8·2	0·01148	0·00153	0·00156
6	8·2	0·01225	0·00077	0·00054
8	7·8	0·01302	—	0·00019

Probable error of a single experiment, 0·00048 gram.

TABLE IVb.—*Absorption of Sodic Hydrate by Wool.*

Sodic hydrate in each bottle = 0·45925 gram.

Weight of anhydrous wool 2·61 (weighed hydrous with 12·7 per cent. of water).

Ash in anhydrous wool, 0·05 per cent.

Equation, $y = 0{\cdot}063086(0{\cdot}31040)^x + 0{\cdot}0053417(0{\cdot}92340)^x$.

$t°$ C.	Time.	Hydrate absorbed.	Remaining hydrate.	Remaining hydrate calc.
—	—	—	0·06843	0·06843
4·0	1·93	0·056671	0·01176	0·01118
,,	2	0·058325	0·01010	0·01063
,,	3	0·060162	0·00827	0·00609
,,	4	0·063147	0·00528	0·00447
,,	6	0·065213	0·00322	0·00337
,,	8	0·065444	0·00298	0·00283
,,	12	0·066591	0·00184	0·00205
,,	20	0·067142	0·00139	0·00109
,,	28	0·067960	0·00046	0·00057
4·5	106	0·068428	—	—

Probable error of a single comparison, 0·00056 gram.

In the following three tables the weight of anhydrous silk in each bottle was 2·75 grams with 8·2 per cent. of moisture and 0·09 per cent. of ash.

TABLE V.—*Absorption of Hydric Sulphate by Silk.*

Hydric sulphate in each bottle, 0·562575 gram.

Equation, $y = 0{\cdot}01225(0{\cdot}58980)^x$.

$t°$ C.	Time.	Sulphate absorbed.	Remaining sulphate.	Remaining sulphate calc.
—	—	—	0·01225	0·01225
6·7	2	0·007583	0·00467	0·00426
,,	3	0·009901	0·00235	0·00251
,,	4	0·010869	0·00136	0·00148
,,	8	0·012251	—	0·00018

Probable error of a single experiment, 0·00021 gram.

TABLE VI.—*Absorption of Hydric Chloride by Silk.*

Hydric chloride in each bottle, 0·41810 gram.
Equation, $y = 0{\cdot}01511(0{\cdot}3134)^x$.

Time.	$t°$ C.	Chloride absorbed.	Remaining chloride.	Remaining chloride calc.
—	—	—	0·01511	0·01511
1	4·5	0·010455	0·00466	0·00474
2	,,	0·013581	0·00153	0·00148
3	,,	0·014735	0·00038	0·00047
4	,,	0·015114	—	0·00015

Probable error of a single experiment, 0·00008 gram.

TABLE VII.—*Absorption of Sodic Hydrate by Silk.*

Sodic hydrate in each bottle, 0·45925 gram.
Equation, $y = 0{\cdot}06200(0{\cdot}4595)^x$.

Time.	$t°$ C.	Hydrate absorbed.	Remaining hydrate.	Remaining hydrate calc.
—	—	—	0·06200	0·06200
1	4·5	0·03444	0·02756	0·02849
2	,,	0·04879	0·01371	0·01309
3	,,	0·05603	0·00597	0·00602
4	,,	0·06071	0·00129	0·00276
5	,,	0·06200	—	0·00127

Probable error of a single comparison, 0·00076 gram.

The weight of cotton referred to in the following three tables was, anhydrous cotton 2·893 grams (weighed hydrous, 3 grams), with 6·9 per cent. of moisture and 0·05 per cent. of ash.

TABLE VIII.—*Absorption of Hydric Sulphate by Cotton.*

Hydric sulphate in each bottle = 0·562575 gram.

$t°$ C.	Time.	Sulphate absorbed.	Remaining sulphate.
—	0	—	0·0049506
4	1	0·0025316	0·0024190
,,	2	0·0042193	0·0007313
,,	3	0·0049506	—

TABLE IX.—*Absorption of Hydric Chloride by Cotton.*

Hydric chloride in each bottle = 0·41810 gram.

$t°$ C.	Time.	Chloride absorbed.	Remaining chloride.
—	—	—	0·007336
4	1	0·0048909	0·002445
,,	2	0·0061136	0·001223
,,	3	0·0073363	
,,	4	No increase.	
,,	6		
,,	8		
,,	10		
,,	12		
,,	20		
,,	193		

TABLE X.—*Absorption of Sodic Hydrate by Cotton.*

Sodic hydrate in each bottle = 0·45925 gram.

Equation, $y = 0{\cdot}012205(0{\cdot}87837)^x + 0{\cdot}016265(0{\cdot}03815)^x$.

$t°$ C.	Time.	Sodic hydrate absorbed.	Remaining hydrate.	Remaining hydrate calc.
—	—	—	0·02847	—
5	1	0·01837	0·01010	0·01134
,,	2	0·01903	0·00944	0·00944
,,	3	0·02020	0·00827	0·00827
,,	4	0·02204	0·00643	0·00727
,,	6	0·02847	—	0·00561

Probable error of a single comparison, 0·00196 gram.

Part II.

The object of the following experiments is to determine the ratio of absorption of different acids by wool and silk from different mixtures of acids. For this purpose we made three mixtures of hydric sulphate and hydric chloride in the following proportions :—

	Gram per c.c.	
(1.) $H_2SO_4 : HCl$	0·001563	sulphate.
	0·00058397	chloride.
(2.) $H_2SO_4 : 2HCl$	0·00117	sulphate.
	0·000876	chloride.
(3.) $H_2SO_4 : 4HCl$	0·00078	sulphate.
	0·001168	chloride.

These mixed acids were made from hydric sulphate and chloride (of the same strength or acidity) in the proportion of 2 : 1, 1 : 1, and 1 : 2 by volume; so that all these mixtures have the same strength as the original or unmixed acids. The acids were of the same strength as in the previous experiments, viz. :—

	Gram per c.c.
Hydric sulphate.....	0·00234
Hydric chloride.....	0·0017519

The wool and silk employed were part of the samples referred to in Part I.

Our method of experiment was as follows :—

In a measured volume (250 c.c.) of mixed acids a known weight (3 grams) of silk or wool was digested in a stoppered bottle for a known length of time at a constant temperature.

After taking out the tissue from the bottle, a measured quantity (25 c.c.) of the acids in the bottle was titrated with sodic hydrate solution, phenolphthaleïn being the indicator.

The sodic hydrate solution was made to have the same strength as the acid solutions; it had been prepared from metallic sodium, and was free from chlorine. This titration gives the total acid absorbed.

The titrated solution containing a trace of soda in excess was now carefully neutralised by adding a few drops of carbonic water (1 c.c. of which happened to correspond with 18 c.c. of soda solution).

When the faint pink colour of the solution had disappeared the solution was titrated with argentic nitrate solution, using neutral potassic chromate as an indicator.

This titration gives the amount of hydric chloride absorbed, which, when subtracted from the total amount of absorbed acid, gives the amount of hydric sulphate absorbed.

The ratios of the number of c.c. of hydric sulphate and twice that

of hydric chloride thus found, give directly the ratio of these two acids in terms of their formulæ as weights.

(α.) *Proportion of Acids*, H_2SO_4 : HCl.

	Units of time.	Temp. corr.	Hydric chloride absorbed, c.c.	Hydric sulphate absorbed, c.c.
Wool	0	—	—	—
Experiment No. 1	2	10·7	4·5	31·75
	0	—	—	—
Wool	3	10·9	5·8	31·7
Experiment No. 2	—	—	4·6	32·9
„ „	—	—	5·0	32·5
„ „	—	—	4·6	32·9
Mean	..	..	5·0	32·5
Silk	0	—	—	—
„	3	11·8	0·87	6·63
„	—	—	0·87	6·63

Ratio of Absorption.

		Formulæ as weights.		Weight.		Volume.	
		H_2SO_4.	HCl.	Sulphate.	Chloride.	Sulphate.	Chloride.
	Acid employed	100	100	100	37·24	100	50
Wool No. 1	Acid absorbed	100	28·34	100	10·57	100	14·17
Wool No. 2	—	100	30·8	100	11·5	100	15·4
Silk ..	—	100	29·3	100	10·91	100	12·98

(β.) *Proportion of Acids*, H_2SO_4 : 2HCl.

	Units of time.	Temp. corr.	Hydric chloride absorbed, c.c.	Hydric sulphate absorbed, c.c.
Wool	0	—	—	—
Experiment (a)	2	11·0	11·25	22·5
Wool	0	—	—	—
Experiment (b)	3	10·9	11·5	25·5
Silk	0	—	—	—
„	3	11·8	2·5	5·0
„	—	—	2·5	5·0

Ratio of Absorption.

		Formulæ as weights.		Weight.		Volume.	
		H_2SO_4.	HCl.	Sulphate.	Chloride.	Sulphate.	Chloride.
	Acid employed	100	200	100	74·5	100	100
Wool (*a*)	Acid absorbed	100	100	100	37·24	100	50
Wool (*b*)	„	100	90·2	100	33·59	100	45·1
Silk ..	„	100	100	100	37·24	100	50

(γ.) *Proportion of Acid*, H_2SO_4 : 4HCl.

	Units of time.	Temp. corr.	Hydric chloride absorbed, c.c.	Hydric sulphate absorbed, c.c.
Wool	0	—	—	—
Experiment (A)	2	10·7	Lost	Lost
Wool	0	—	—	—
Experiment (B)	3	10·9	16·56	18·44
Silk	0	—	—	—
„	3	11·8	3·5	4·0

Ratio of Absorption.

		Formulæ as weights.		Weight.		Volume.	
		H_2SO_4.	HCl.	Sulphate.	Chloride.	Sulphate.	Chloride.
	Acid employed	100	400	100	148·3	100	200
Wool (A)	Acid absorbed	—		—		—	
Wool (B)	„	100	179·6	—		—	
Silk ..	„	100	175·0	—		—	

The above results show that although the absolute amounts of absorption are different, the ratios of absorption are the same for wool and silk.

On account of the very small absorption by cotton of the individual acids (see Tables VIII and IX), we did not submit that material to the action of their mixtures.

Summary.

Table XI.

Tissue.	Reagent.	Weight of reagent.	Maximum absorption per gram of anhydrous tissue.	Reference to tables.	Weight of anhydrous tissue.
		gram.	gram.		gram.
Wool...	Hydric sulphate	0·18754	0·018263	II*a*.	0·8728
„ ...	„ „	0·66256	0·023988	II*b*.	2·6100
„ ...	„ chloride	0·41810	0·015927	III.	2·6100
„ ...	Sodic hydrate ..	0·07654	0·014913	IV*a*.	0·8728
„ ...	„ „ ..	0·45925	0·026218	IV*b*.	2·6100
Silk	Hydric sulphate	0·56258	0·004455	V.	2·7500
„	„ chloride	0·41810	0·005495	VI.	2·7500
„	Sodic hydrate ..	0·45925	0·022545	VII.	2·7500
Cotton..	Hydric sulphate	0·56258	0·00171	VIII.	2·893
„ ..	„ chloride	0·41810	0·00254	IX.	2·893
„ ..	Sodic hydrate ..	0·45925	0·00984	X.	2·893

The mean probable error of a single comparison with experiment of our calculated nine equations is 0·00075 gram, or about 2 per cent. on the mean total absorption. As this is about the ordinary error of careful work with small quantities, we infer that the absorptions we have measured are amenable to laws already established in other fields of chemical investigation. Combination proceeds at first with considerable absolute rapidity, and continues with decreasing rapidity. Increase in the mass of reagent—which as a rule accelerates combination—may be counterbalanced by lowering the temperature (Tables IVa and IVb).

From the column "maximum absorption per gram" in Table XI, it is easy to calculate that the ratios of such absorption in the last six (comparable) experiments are—

	Cotton.		Silk.
Hydric sulphate	1	:	2·6
Hydric chloride	1	:	2·2
Sodic hydrate.....	1	:	2·3

numbers exhibiting a significant tendency to identity in the case of all three reagents.

Lines 5 and 8 in the same table show that wool and silk also tend to resemble each other in the weight they absorb of sodic hydrate; but

from the remainder of the table it is clear that wool takes up much more from acid solutions than is the case with silk.

The quantities 0·41810 gram hydric chloride and 0·45925 gram sodic hydrate in the same table are in the ratio HCl : NaHO. When wool is treated with the weak reagents severally in this proportion, the absorption is nearly in the ratio 2HCl : 3NaHO. The corresponding results for silk and cotton are 3HCl : 10NaHO in both cases. There is thus a very intimate relation between silk and cotton—a relation which, whatever it may be in part, is shown by these changes to be, to a great extent, of a strictly chemical nature.

We have, in conclusion, to express the hope that our investigation, while bearing on the one hand on questions of great technical importance, may not be without its value in the profounder future study of cotton, silk, and wool—three bodies of definite chemical composition, but whose intimate constitution still remains obscure.

XXI.—*On the Action of Chlorine on Certain Metals.*

By Richard Cowper, A.R.S.M., Demonstrator in the Laboratory of the Royal Naval College.

In performing the ordinary experiment of burning sodium in chlorine, I observed that with a more than usually dry sample of the gas, the bright surface of the melted metal tarnished very slowly; and it occurred to me that if the chlorine were in a perfectly dry condition it might have no action, and also that this might be true in the case of other metals said to combine directly with chlorine at ordinary temperatures.

I have since found that this inability of dry chlorine to act on sodium has been observed by Wanklyn (*Chem. News*, **20**, 271), who has not, however, so far as I can discover, pursued the experiment with other metals.

I proceeded as follows:—

Chlorine was prepared by the action of pure hydrochloric acid on manganese dioxide. The gas was passed through three wash-bottles containing water to free it from hydric chloride, and then through tubes of from $\frac{3}{4}$-inch to 1-inch diameter, having an aggregate length of about 8 feet, closely packed with anhydrous porous calcium chloride.

It is well known that if Dutch metal be introduced into a vessel containing chlorine prepared in the usual manner, combustion takes place with evolution of light and heat. It was found that chlorine

prepared and dried in the manner above described acted very slowly on Dutch metal.

Some Dutch metal was next placed with a piece of freshly fused calcium chloride in a small thin glass tube and sealed. This small tube was placed in a much larger tube, also containing some pieces of freshly fused calcium chloride. The larger tube was then filled with chlorine dried by passage through calcium chloride tubes, then sealed, and allowed to stand for several days. The small tube was then broken by shaking, and the metal thus exposed to the chlorine. It was found that the Dutch metal remained bright. (A specimen thus prepared is still apparently unacted on after about three months.)

On introducing a minute quantity of water into the tube, the chlorine was rapidly absorbed. If a drop of water were allowed to come in contact with the metal, the action was instantaneous and accompanied by evolution of light and heat.

When chlorine, dried by passage through calcium chloride tubes, was brought in contact with dry metallic zinc in the form of thin foil, the latter was distinctly acted on, assuming a moist appearance; but this was not the case when the chlorine had stood for some days in contact with freshly fused calcium chloride.

It was observed that the zinc was most acted on by the partially dried chlorine at the point where the gas first came in contact with the metal. A glass tube about 18 inches in length was closely packed with pieces of thin zinc-foil, and chlorine dried by calcium chloride was passed through it. It was found that the action, as indicated by the moistening of the surface of the metal, extended but a very short distance from the end at which the gas was admitted, the greater part of the zinc remaining dry and bright. Metallic zinc, therefore, appears to offer a highly advantageous means of removing the last traces of moisture from chlorine.

Experiments were made with the following metals, the chlorine in each case being allowed to stand in contact with pieces of freshly fused calcium chloride in a sealed tube during several days, in the manner already described:—

Magnesium, in the form of wire, was not attacked.

Silver, in the form of leaf, was acted on very slowly. The presence or absence of light appeared to make no difference in the rate at which the metal was attacked.

Bismuth was at first apparently unacted on. After several days, a specimen in the form of coarse powder had become slightly tarnished, but the atmosphere in the tube remained quite yellow.

Tin, in the form of foil, was rapidly attacked with evolution of heat.

Antimony and arsenic, in the state of powder, were acted on immediately, with evolution of light and heat.

It may be noted that these last three elements produce chlorides which are liquid at ordinary temperatures.

Mercury appeared to be acted on by the dry chlorine as rapidly as by the moist gas.

It has been observed by Wanklyn, as mentioned above, that sodium is not acted on by dry chlorine, either at ordinary temperatures or when melted in contact with the gas.

I made the following experiment:—A piece of sodium was placed in a glass tube. Chlorine, dried over calcium chloride, was passed through the tube, and the piece of sodium was heated to dull redness. It was then allowed to cool in the current of chlorine, and the tube was sealed. The sodium was then raised to the melting point, and shaken so as to cause the metal to flow from its slag-like envelope. At first it became dulled; but after several times causing a fresh surface to be exposed to the chlorine, it remained bright, the atmosphere in the tube being at the same time quite yellow, showing that very little chlorine had been absorbed. The action observed on first exposing a bright surface of melted sodium to the chlorine is no doubt due to the gas being imperfectly dried.

If dried chlorine be passed over a piece of potassium, the latter catches fire. This is, however, probably due to the heat caused by the action of the chlorine on the envelope of KHO, which surrounds the piece of potassium.

Some potassium was next sealed up in a tube containing dry air. The metal was then heated until all the oxygen was absorbed, and a bright surface of potassium obtained. The tube was then filled with chlorine, dried by passage first through calcium chloride tubes, and then through a tube packed with thin zinc-foil. The potassium at first remained bright, but slowly became covered by a film of a rich purple colour. This is no doubt the sub-chloride described by Rose (*Pogg. Ann.*, **121**).

The action was much accelerated by raising the metal to its melting point. The potassium did not, however, burn until the temperature greatly exceeded the point of fusion.

If the purple compound be heated *in vacuo*, it is decomposed, metallic potassium and potassium chloride being apparently formed.

If a minute quantity of water be introduced into a tube containing potassium and chlorine, the latter is rapidly absorbed.

XXII.—*Some Notes on Hydrated Ferric Oxide and its Behaviour with Hydrogen Sulphide.*

By Lewis T. Wright.

For the purpose of studying some points in the reaction between hydrogen sulphide and hydrated ferric oxide, I had occasion to prepare some of the latter material by precipitation of ferric hydrate from a ferric chloride solution by means of liquid ammonia in the usual way; but I did not find it possible in this manner to prepare a material perfectly free from basic chloride. I used both the method of pouring excess of liquid ammonia into ferric chloride solution, and that of pouring ferric chloride solution into excess of liquid ammonia, and always experienced that the resulting precipitates of ferric hydrate, when washed most exhaustively with boiling water with the aid of a filter-pump, never failed to yield minute traces of chlorine even in the last washings.

After many washings, the filtrates cease to yield any decided precipitate with silver nitrate, but continue to give a persistent opalescence indicative of minute traces of chlorine. On drying the washed ferric hydrate at about 100° in a water-bath for a few hours, and again washing with boiling water, the first portions of the wash-water give a strong chlorine reaction, showing that in the process of drying some basic chloride has been dissociated. I have also noticed that the first washings are acid, as might be supposed if basic chloride had been dissociated. On repeating the drying and washing of the ferric oxide in the same manner as before, I found that the wash-water gave both acid and chlorine reactions.

In order to avoid the great inconvenience of handling a bulky gelatinous precipitate, I thought to obtain a material in a more compact form by the following method of preparation.

Ferric chloride solution was added slowly to excess of liquid ammonia, with constant stirring. This operation was effected in a porcelain evaporating dish, which was then placed in a water-bath, and its contents evaporated to dryness. By this means, a dirty red-brown mass was obtained, showing here and there patches of ammonium chloride. This mass, on being treated with water, fell mostly into an impalpable powder, a large portion of which, on attempted filtration, passed through the filter-paper and even through many successive filters. The filtrates were of bright red colour, and when dilute, had in certain lights a purple appearance, suggestive of the purple colour of ignited ferric oxide. Each filtrate, on being boiled

and refiltered, left on the paper a small quantity of red hydrated ferric oxide, but the filtrate was still red. Portions of these red filtrates, which all had an acid reaction, on treatment with a little ammonia to alkaline reaction and boiling, partially coagulated, and left decided quantities of bright red powder on the filter, but the filtrates were still red, not having the appearance of solutions, being muddy and opaque, with what appeared to be an unfilterable precipitate. This is probably similar to the material called "colloïdal ferric hydrate," "dialysed iron," or "fer Bravais." Magnier de la Source (*Compt. rend.*, **90**, 1352—1354) in describing a similar condition of ferric hydrate, or compound of ferric hydrate and ferric chloride, supposes that under certain conditions ferric hydrate is soluble in water; but I cannot think that this is a case of true solution, but rather of "pseudo" solution; for the filtrates I obtained had all the appearance of holding in suspension an intensely impalpable powder. They deposited small quantities of red powder on standing for some weeks, and in cases where they had been treated with ammonia and boiled to neutrality, they exhibited after long standing an acid reaction. Now, however, a drop of liquid ammonia and the application of a little heat, caused the pseudo solution to coagulate in light red flocks, which speedily settling, left the supernatant liquor perfectly bright and clear. I have made some further observations which may explain the presence of basic salt in the ferric hydrate prepared in presence of ammonium chloride, and on the difficulty of preparing ferric hydrate free from basic salt.

Some ferric hydrate washed, dried at 100°, rewashed and redried at 100°, lost on ignition—

(1.) 11·49 per cent.	$Fe_2O_3H_2O$
(2.) 11·32 „	10·11 per cent.

1 gram of this hydrated ferric oxide boiled with about 100 c.c. of pure water in a retort, gave a distillate quite neutral to litmus.

5 grams NH_4Cl in 100 c.c. pure water on boiling gave a weak acid distillate. On pouring the ammonium chloride solution into the retort containing the hydrated ferric oxide, and distilling to dryness, free ammonia equal to 0·005 gram was obtained. On repeating this experiment many times, I always obtained an alkaline distillate containing an appreciable quantity of ammonia, the action—

$$Fe_2Cl_6 + 6NH_3 + 6H_2O = Fe_2H_6O_6 + 6NH_4Cl$$

being apparently reversed—

$$Fe_2H_6O_6 + 6NH_4Cl = Fe_2Cl_6 + 6NH_3 + 6H_2O.$$

Having prepared numerous samples of hydrated ferric oxide by means of Fe_2Cl_6 and NH_3, I have noticed that they all possess different

shades of colour, no two samples having exactly the same shade of red. They range in colour from dirty brown to bright brick-red. D. Tommasi (*Bull. Soc. Chim.* [2], **38**, 152—153) divides ferric hydrate into two classes: red, obtained by precipitating a ferric salt with alkalis, and yellow, by oxidation of ferrous hydrate, ferrosoferric hydrate, or ferrous carbonate; but (*Bull. Soc. Chim.* [2], **37**, 196—197) he has found that ferric hydrate kept under water for a year is converted to the extent of 0·3 per cent. into a soluble modification identical with Graham's "colloïdal hydrate."

I am inclined to think that his ferric hydrate was slightly impure, and that the colour differences and the formation of a small quantity of "colloïdal hydrate" are due to contained basic salt.

The object I had in view, viz., the study of the reaction between ferric hydrate and hydrogen sulphide was much hampered by the impurity of the ferric hydrate, and also by want of uniformity between the various samples I had prepared.

Recently precipitated ferric hydrate in the gelatinous state suspended in water, on being saturated with hydrogen sulphide, becomes black, and is completely soluble in excess of potassium cyanide, with formation of potassium ferrocyanide and sulphide: $FeS + 6KCN = K_2S + K_4Fe(CCN)_6$, but ferric hydrate washed and dried at 100° does not behave in quite the same manner, being more or less converted into a form of ferric oxide inactive with H_2S. Tommasi found that ferric hydrate kept under water for a year became converted to the extent of 30 per cent., into a modification insoluble in dilute acids. Some portions of the filtrates before spoken of containing "colloïdal hydrate" remained quite unchanged in colour when saturated with hydrogen sulphide. Others retained a bright red colour for ten minutes after the solution was saturated with hydrogen sulphide, and then suddenly flashed off black. On standing a few moments, black flocks collected, and settling left the solution bright and colourless, or slightly yellow. On boiling with potassium cyanide, the black flocks were dissolved; but particles of purple-red ferric oxide were left undissolved. This was a form inactive to hydrogen sulphides. Some portions of the filtrates containing "colloïdal hydrate," which deposited black flocks on treatment with hydrogen sulphide were filtered. Sometimes the filtrate was quite colourless, and after standing became opalescent from decomposing hydrogen sulphide. Others passed through of a slight yellow colour, and on boiling deposited black flocks of ferrous sulphide, and on filtration gave colourless filtrates, becoming opalescent on standing. On boiling, this opalescent water became quite clear, the free sulphur being removed, probably thus:—

$$H_2O + S = H_2S + O.$$

Cross (*Chem. Soc. J.*, 1879, **1**, 250) has noticed an action similar to this, to which I shall have again to refer.

These previously opalescent filtrates now contained iron in solution as ferrous sulphate,

(1.) 0·112 gram Fe per 1000 c.c.
(2.) 0·126 „ „ „

which was estimated with potassium dichromate after expulsion of all hydrogen sulphide.

As a general rule, on boiling the iron sulphide suspended in water (produced by treating ferric hydrate suspended in water with excess of hydrogen sulphide), it is found impossible to finally expel all hydrogen sulphide from solution whilst any iron sulphide (ferrous sulphide?) remains, for hydrogen sulphide is continually being generated and ferrous sulphate formed.

Supposing the ferric hydrate to react with hydrogen sulphide in the following manner:—

$$Fe_2H_6O_6 + 3H_2S = 2FeS + S + 6H_2O,$$

some of the free sulphur decomposes water in the manner noticed by Cross (*loc. cit.*),

$$4S + 4H_2O = 3H_2S + H_2SO_4.$$

the sulphuric acid reacting with the ferrous sulphide, thus:—

$$H_2SO_4 + FeS = FeSO_4 + H_2S.$$

There are two equations in use in text-books for the purpose of explaining the reaction between hydrated ferric oxide and hydrogen sulphide, a reaction largely made use of in gasworks for removing the latter from crude coal-gas. They are:

(A.) $Fe_2O_3,H_2O + 3H_2S = Fe_2S_3 + 4H_2O.$
(B.) $Fe_2O_3,H_2O + 3H_2S = 2FeS + S + 4H_2O.$

If either one of these two reactions took place alone, it would be easy to decide which of the two did actually occur: for if the reaction proceeded according to equation (A) no free sulphur would be found; if, according to the equation (B), then free sulphur equal to one-third of the total sulphur entering into action would be found in the free state.

In my experiments I have always found free sulphur as one of the products of the reaction. By treating Fe_2O_3,H_2O, suspended in bisulphide of carbon with gaseous hydrogen sulphide, and filtering the clear bisulphide after the black iron sulphide has settled, I have

obtained very appreciable quantities of sulphur. I mixed $Fe_2O,3H_2O$ with powdered quartz for the purpose of moderating the reaction, and placed it in tubes. From the tubes the air was expelled by a current of hydrogen, and then hydrogen sulphide was passed through. When the ferric oxide appeared saturated, hydrogen was again passed through the tubes to expel the excess of hydrogen sulphide; and then without contact with air the material was washed with pure carbon bisulphide. When the washing was complete, the material was turned out of the tubes and exposed to the air until the oxidation was complete. The material was again washed with carbon bisulphide, the washings were evaporated, and the free sulphur was weighed. In this manner I obtained the following numbers :—

	Free sulphur before oxidation. gram.	Free sulphur formed by oxidation. grams.
(1.).....	0·020	3·100
(2.).....	0·100	1·400
(3.).....	0·100	3·500
(4.).....	0·035	0·271
(5.).....	0·005	0·203

The sulphur in the free state before oxidation does not appear to bear any relation to the sulphur produced by the oxidation of the iron sulphide or sulphides.

I have noticed also, in the case of the hydrated ferric oxide used in coal-gas purification, that the free sulphur produced in the reaction between Fe_2O_3 and H_2S is about one-fifteenth to one-thirtieth of that formed on the oxidation of the "fouled oxide."

It might be supposed that all the free sulphur formed in the reaction between Fe_2O_3 and H_2S was not soluble in carbon bisulphide. This I do not think probable, for then it would be necessary to assume that the insoluble sulphur became converted into the soluble variety during the oxidation of the sulphide; otherwise the oxide material used in gasworks would accumulate large quantities of insoluble sulphur, which is not the case in my experience.

For the purpose of further studying the nature of the reaction, I carefully estimated the water formed. This, of course, does not affect the question as to which reaction, (A) or (B), takes place, or whether both occur, for the quantity of water formed in each case is the same. The ferric oxide used lost on ignition 10·15 per cent., 10·09 per cent., 10·13 per cent., 10·10 per cent., and therefore closely approximated to the hydrate Fe_2O_3,H_2O. It had been finely powdered, dried at 100°, and was kept in a desiccator over concentrated sulphuric acid. A **U**-tube fitted with glass stopcocks was weighed full of dry hydrogen,

some Fe_2O_3,H_2O placed in the bend, and the tube again filled and re-weighed with dry hydrogen. Another similar **U**-tube, charged with powdered calcic chloride and weighed full of hydrogen, was connected with the outlet of the first **U**-tube. Sulphuretted hydrogen (containing 15 to 20 per cent. hydrogen) washed and dried through two drying cylinders charged with powdered calcic chloride, was now passed through the two **U**-tubes, the first, containing the Fe_2O_3,H_2O, being immersed in a beaker of cold water to moderate the action. When the action appeared to be complete, that is to say, when the whole of the material in the first **U**-tube was quite black, the cold water in the beaker was changed for boiling water, and the current of hydrogen sulphide replaced by dry hydrogen to expel excess of hydrogen sulphide. The hot water in the beaker was changed for cold, and when sufficient time had elapsed to enable the first **U**-tube to become cold, the stopcocks were closed and the tubes weighed separately. The increase in weight of the two tubes was taken as the quantity of hydrogen sulphide which had entered into action. The increase in weight of the calcium chloride tube was taken as the 3 mols. of water formed by the reaction, and the 1 mol. expelled from the hydrated $Fe_2O_3H_2O$ which had entered into action, according to the equations—

$$\text{(A.)}\quad Fe_2O_3,H_2O = Fe_2S_3 + 4H_2O.$$
$$\text{(B.)}\quad Fe_2O_3,H_2O = 2FeS + S + 4H_2O.$$

The results I obtained are embodied in the following table which contains the following particulars:—

(1.) The weight of Fe_2O_3,H_2O operated upon.

(2.) The weight of above after treatment with hydrogen sulphide, and drying in a current of hydrogen at about 100°.

(3.) Difference between (1) and (2).

(4.) The water resulting from the reaction.

(5.) The weight of hydrogen sulphide entering in action obtained by adding (3) and (4).

(6.) The weight of hydrogen sulphide with which the Fe_2O_3,H_2O was theoretically capable of reacting according to equations (A) and (B).

(7.) The percentage of Fe_2O_3,H_2O entering into action calculated from (5) and (6).

(8.) The ratio $\frac{3H_2S}{4H_2O}$, or $\frac{\text{increase in weight of both tubes}}{\text{increase in weight of calcium chloride tube}}$, or $\frac{(5)}{(4)}$.

(9.) Sulphur calculated from (5).

(10.) Sulphur by analysis. This was not ascertained in all cases, for the products of the reaction were used for other inquiries.

(11.) Sulphur found in the free state by washing the product of reaction with carbon bisulphide in the manner usual in such cases, but without access of air.

	Weight of $Fe_2O_3H_2O$.	Weight after treatment with H_2S.	Increase of weight.	Water collected in $CaCl_2$ tube.	H_2S entering into action.	Possible amount of H_2S.	Percentage of $Fe_2O_3H_2O$ entering into action.	$\frac{3H_2S}{4H_2O}$.	Sulphur in residue calculated.	Sulphur in residue found.	Sulphur in free state.
	grams.	grams.	gram.	gram.	gram.	gram.			gram.	gram.	gram.
1.....	1·357	1·540	0·183	0·487	0·670	0·778	86·1	1·376	0·630	—	—
2.....	1·015	1·183	0·168	0·370	0·538	0·582	92·5	1·427	0·506	0·518	—
3.....	1·035	1·198	0·163	0·350	0·513	0·593	86·5	1·465	0·483	0·480	—
4.....	0·790	0·923	0·133	0·265	0·398	0·453	87·9	1·502	0·375	0·380	—
5.....	0·678	0·774	0·096	0·233	0·329	0·389	84·6	1·412	0·310	—	—
6.....	1·560	1·779	0·219	0·474	0·693	0·894	77·5	1·462	0·652	—	0·037
7.....	1·320	1·518	0·198	0·490	0·688	0·756	91·0	1·404	0·647	0·637	0·035
8.....	1·204	1·396	0·192	0·400	0·592	0·690	85·8	1·480	0·557	—	0·056
9.....	1·255	1·442	0·187	0·445	0·632	0·719	87·9	1·420	0·595	—	0·050
							Average	1·438			

The numbers representing the ratio $\frac{3H_2S}{4H_2O}$ are not quite so sharp as I expected, or was justified in expecting, for the greatest possible care was observed in all the experiments. The average ratio, $\frac{3H_2S}{4H_2O}$, found, 1·438 is slightly higher than theory 1·417. In six experiments it is higher, in three experiments lower. This might be perhaps because the sulphides retained a little water, but I do not quite understand why this should be so in some cases and not in others.

Assuming that the free sulphur found was produced according to the equation (B), then it would appear that from 17 per cent. (Experiment 6) to 30 per cent. (Experiment 8) of the Fe_2O_3,H_2O entering into action went to form ferrous sulphide, FeS, and that the remaining portion formed ferric sulphide, Fe_2S_3, according to equation (A). The sulphides formed in the dry way by the action of H_2S on Fe_2O_3,H_2O, as in my experiments, as well as the sulphides prepared in the wet way by precipitation of neutral ferrous salts with hydrogen sulphide, or by adding a neutral ferric salt slowly to a solution of ammonium sulphydrate, are all soluble in hot potassium cyanide solution, with production of potassium ferrocyanide. They are completely decomposed by neutral cupric sulphate or silver nitrate. My experiments in this direction are at present too incomplete to be used in any way for the purpose of explaining the composition of the sulphides formed by means of H_2S and $Fe_2O_3H_2O$; but I think that the amount of water affords strong evidence that the reaction proceeds according to either one or both of the equations (A) and (B),

and that the amount of free sulphur indicates that both occur, the former (A) predominating, but they do not bear any definite relation to each other in amount, but vary in proportion to each other with slightly varying circumstances, which I have not determined, and upon which I can throw no light. However, I think it possible that further inquiry by means of the decompositions of the sulphides with cupric sulphate and silver nitrate may definitely prove the composition of the sulphide formed in the reaction between Fe_2O_3,H_2O, and H_2S.

The mixture of ferrous and ferric sulphides, as obtained in my experiments, is intensely pyrophoric, firing with the very first contact of air. On this account extraordinary precautions had to be observed, whilst the material was in the dry state; after it had been moistened with water, however, the oxidation was by no means so rapid.

The action of potassium cyanide on these iron sulphides is a useful means of distinguishing between the forms of ferric oxide active or inactive with sulphide, for any ferric oxide unacted upon by hydrogen sulphide or dilute potassium sulphide is left undissolved, and can be thus separated and estimated. To effect the solution of the ferrous and ferric sulphides it is necessary to boil them for about ten minutes with an excess of potassium cyanide. If, however, they be boiled with an insufficient amount of potassium cyanide, a curious action takes place. On filtering off the liquor from the undissolved sulphide, the filtrate runs through of a clear yellow colour; but on attempting to wash the undissolved sulphide with water, it immediately passes through the filter-paper in a similar condition to the "colloidal" ferric hydrate before spoken of. The filtrate is then thick and muddy, and quite black and opaque. On standing for some time, black flocks are deposited, and the solution partially clears. I have noticed the same appearance when cupric sulphide has been treated with an amount of potassium cyanide insufficient to effect its solution.

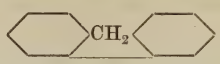
XXIII.—*Note on some Derivatives of Fluorene*, $C_{13}H_{10}$.

By W. R. Hodgkinson and F. E. Matthews.

The hydrocarbon, isolated from coal-oil by Berthelot (*Ann. Chim. Phys.* [4], **12**, 222), and termed *fluorene* from its supposed fluorescent property, has been investigated by several chemists, and its constitution as *o*-diphenylenemethane determined by its production from diphenylmethane by passing through a red-hot tube (Graebe, *Annalen*,

174, 194), and the reduction of diphenyleneketone by zinc-dust or phosphonium iodide (Fittig, *Ber.*, **6**, 187 ; Graebe, *Ber.*, **7**, 1625).

Its constitution would therefore be expressed by—



More recently, however, Carnelley (*C. J.*, **37**, 708) has discussed the constitution of coal-tar fluorene, and the fluorene from diphenyleneketone, and notices that of the six possible isomerides of this body several occur in coal-oil, and several are also formed when the vapours of benzene and toluene are passed through a heated tube.

The object we had in view in commencing this investigation was in the first place to obtain the phenol or hydroxy-derivative, fluorol, $C_{13}H_{10}O$, as a starting point for further work.

As diphenylene ketone is somewhat difficult to obtain in quantity, and the yield of the hydrocarbon from it is by no means a quantitative one, we have employed coal-tar fluorene obtained from Kahlbaum in a state of approximate purity. For further purification it was distilled, and the fraction between 300—310° crystallised five or six times from alcohol, reserving only the crystals falling out between 25° and 30°. Thus purified, it melts constantly at 113°, and the slight fluorescence may be almost entirely removed by one or two crystallisations from glacial acetic acid, or by sublimation over potassium carbonate.

Glacial acetic acid is by far the best solvent from which to crystallise fluorene. By means of this solvent, it is possible to separate from fluorene boiling between 300—310°, hydrocarbons melting at 112—113° ; 124° ; 118° ; and, in small quantity only, at about 200°.

The one melting at 118°, and occurring in pretty large quantity in coal-tar fluorene, is most probably the γ-methylene-diphenylene of Carnelley. It certainly gave another body in addition to diphenyleneketone on oxidation ; we have not, however, examined these substances further, as we desired only the ortho-modification.

The product we have employed oxidises in glacial acetic solution completely with chromic acid to diphenylene ketone, no quinone being produced.

On analysis 0·1106 gram gave 0·3796 gram CO_2 and 0·0645 gram OH_2.

			Found.
C_{13} = C....	93·97	C....	93·60 per cent.
H_{10} = H ..	6·03	H ..	6·47 ,,

The *α-dibromofluorene*, $C_{13}H_8Br_2$, was made by dissolving the hydrocarbon in chloroform, adding a slight excess of bromine, and leaving the chloroform to evaporate spontaneously. The compound is almost

insoluble in cold alcohol, but dissolves easily in boiling alcohol, from which solution it separates in *almost* colourless tabular crystals. From hot glacial acetic solution it forms perfectly colourless crystals melting at 165°. Light causes the crystals to become slightly yellow.

A bromine determination by heating with Iceland spar gave—

$$\text{49·71 per cent. Br.} \quad \text{Theory } \begin{matrix} C_{13} \\ H_8 \\ Br_2 \end{matrix} = \text{Br 49·38.}$$

We did not notice any formation of the β- and δ-dibromofluorenes as noticed by Lehmann and Azruni; also by Fittig and Schmitz. Their formation may depend on the solvent employed.

Monobromofluorene, $C_{13}H_9Br$.

This substance is formed when bromine is very carefully added to a solution of the hydrocarbon in chloroform, care being taken to keep the temperature as low as possible. The product, even when the fluorene is maintained in excess, still contains the dibromo-compound, from which the mono-derivative may be separated by repeated solution in, and crystallisation from, about 90 per cent. alcohol. It forms colourless needles melting at 101—102°.

Analysis gave 32·65 per cent. bromine; the formula $C_{13}H_9Br$ requires 32·54 per cent.

This substance is exceedingly soluble in cold chloroform.

Both the mono- and di-bromofluorenes yield on oxidation a substituted diphenylene ketone. The product appears to be the same whether chromic acid in glacial acetic or permanganate is used.

Dibromodiphenylene ketone, $C_{13}HBr_2O$.

This is best obtained by oxidising the (165°)-α-dibromfluorene with chromic acid in acetic acid solution. It forms bright yellow microscopic crystals from acetic acid, melting at 198°.

Analysis gave 47·34 per cent. bromine; the formula requires 47·39.

The monobromfluorene, when carefully oxidised with the theoretical amount of chromic anhydride, yields bromdiphenylene ketone, $C_{13}H_7BrO$, in dark yellow needles melting at 104°.

The production of diphenylene ketone alone, by oxidation of the fluorene, and the formation of the dibromo-compound melting at 165°, was sufficiently conclusive that the hydrocarbon we are dealing with had the constitution assumed as that of ortho- or α-methylene-diphenylene.

The sulphonic acid, $C_{13}H_3.SO_3H$, was therefore made by dissolving the hydrocarbon in chloroform and adding the theoretical quantity of sulphuric chlorohydrine, SO_3HCl, to form the monosulphonate.

The action is a very violent one, and requires to be moderated by careful cooling during the operation.

The free acid is a gummy substance very soluble in water. It was neutralised by potassium carbonate, and the salt $C_{13}H_9SO_3K$ was crystallised from warm water, in which it is somewhat less soluble than in cold. It forms microscopic cubic crystals, which are difficult to obtain colourless.

The barium salt is also very soluble in water, from which it separates in very small crystals, containing two molecules of water.

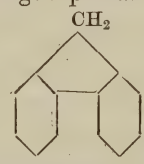
Analysis. Barium Salt.

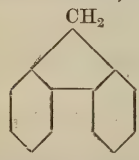
0·974 air dried at 130° gave 0·053 OH_2.
0·921 „ „ 0·343 $BaSO_4$.

	Theory $(C_{13}H_9SO_3)_2Ba + (OH_2)_2$.	Found.
OH_2.....	5·43	5·43
Ba	20·66	20·70

The cadmium salt 0·5 gram gave on drying at 130° 0·0764.
„ „ 1·0 „ 0·2012 gram CdS = 0·1565 I.

Theory $(C_{13}H_9SO_3)_2Cd + 6OH_2$.		Found.	
OH_2....	15·28	OH_2....	15·28 per cent.
Cd	15·77	Cd	15·65 „

It was at first thought probable that the sulphonic group would occupy the position 

to the methylene group in the fluorene molecule, and that on fusion with potassium hydroxide a fluorol, 

, might be obtained.

A considerable quantity of the potassium sulphonate was therefore

* There are as yet no particular grounds on which to base the assumption of the position of the SO_3.

fused at first with slightly aqueous potash, but after a few trials as to the conditions of the reaction, it was fused with dry potash at a temperature a little above 400° C. The operation requires great care, as the reaction takes place within very narrow limits of temperature, below which there is no result, and above which the substance is completely decomposed.

The fused mass, after treating with water and acidification, was repeatedly shaken out with ether and chloroform, which extracted a sparingly soluble substance crystallising, on evaporation of the solvents, in almost colourless needles. The crystals dissolved in aqueous potassium carbonate, and were reprecipitated unchanged by acids.

This substance is almost insoluble in cold water, but readily in hot, and more so in alcohol. From hot aqueous solutions it separates in very brilliant small rhombic prisms, melting at 205°, which become glassy after fusion, and decompose when heated to between 220—230°. Its solution in water gives no coloration with ferric chloride. It forms crystalline nitro- and oxidation-products, which, however, have not yet been analysed.

The yield from the potash fusion, even under the most favourable conditions, is very small, and considerable loss is experienced in separating it from a tarry body formed at the same time, which protects it from the action of the water or potassium carbonate solution employed for extraction. It was afterwards found better to distil the acidified product of the fusion with steam.

The first portions of the steam-distillate came over charged with a white crystalline substance which, on the first crystallisation from hot water, showed itself to be a mixture of crystals of the same form as those obtained by extraction of the fused product with ether-chloroform, with others of much smaller size, and differing from the former in shape and in their solubility in water.

This second body is easily separated from the one previously named, melting at 205°, by its extreme solubility in hot water, and by not separating from this solution until cooled to between 10° and 15°, whereas the body first mentioned is completely deposited, even while the temperature is so high as 30—35°. It forms very small colourless acicular crystals, which melt at about 180°.

The aqueous solution gives no colour-reaction with ferric chloride.

Analysis.

Substance 0·0492 gram gave 0·0234 gram OH_2 and 0·1288 gram CO_2.

		Theory $C_{12}H_{10}O_3$.	
C.....	71·37	C.....	71·28
H	5·28	H	4·25

The quantity of the two trihydroxydiphenyls at our disposal hitherto is not very large, and in consequence we have not been able to try the action of zinc-dust on a scale large enough to give definite results.

Analysis of the Body melting at 204—205°.

I.... 0·0775 substance = 0·2025 CO_2 and 0·0387 OH_2.
II.... 0·0640 „ = 0·1670 „ 0·0290 „

	I.	II.		Theory for $C_{12}H_{10}O_3$.
C....	71·27	71·17	C_{12}	71·28
H ..	5·54	5·00	H_{10}	4·95
			O_3	

Other Analyses, Material not quite Pure.

	III.	IV.
Substance ..	0·0492	0·0448
CO_2.....	0·1282	0·1167
OH_2	0·0237	0·0215
C.....	71·06	71·05 (p. c.)
H	5·35	5·29 „

This was a very extraordinary result, and could scarcely be explained as arising from the reaction of potash with a monosulphate only. The formula $C_{12}H_{10}O_3$ indicates a trihydroxydiphenyl, and such a body could result only from the splitting off of the methylene-group in fluorene, and its replacement by two hydroxyl-groups.

No exactly analogous case of the action of potash occurred to us, but it did not seem very unlikely that the five-carbon ring or group might not be sufficiently stable to be able to resist the action of the fused potash. The hydrocarbon was therefore dropped into potash in a state of fusion (at a pretty high temperature, about 400° C.) in a silver dish. A small quantity volatilised unchanged, the greater part, however, forming a combination of a red colour with the potash, was apparently non-volatile, and floated as a distinct red layer on the excess of fused potash. On cooling and treatment with water, it was at once apparent that several products had been formed, a red substance insoluble in the alkaline solution, together with a little unchanged hydrocarbon, and another body, also of a yellow or red colour, remaining in solution in the alkali. This latter body was precipitated, for the most part, on acidifying the potash solution, as a yellowish flocculent substance, soluble in boiling water, and slowly separating therefrom on cooling in a crystalline form. It was crystallised several times from water, becoming each time less strongly coloured but we have not yet

been able to obtain it quite colourless, which it probably would be if quite pure. We have not yet examined the other products of the fusion.

The substance crystallised from water gives a decided colour reaction with ferric chloride. It melts at 98°, without any decomposition.

Analysis I.

0·1163 gram substance gave 0·3290 CO_2
and 0·0535 OH_2 = C 77·15
H 5·11

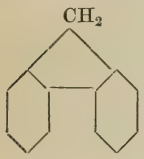
Analysis II.

0·1070 gram substance gave 0·3028 CO_2
and 0·0526 OH_2 = C 77·17
H 5·46

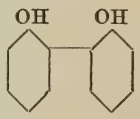
These figures indicate a composition—

$C_{12}H_{10}O_2$. Theory C 77·41
H 5·37

or a dihydroxydiphenyl presumably formed by the splitting off of the methylene-group.



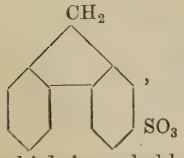
in fluorene, and the introduction of two hydroxyl groups



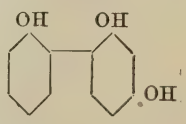
That the fluorene has been reduced to a diphenyl derivative there is little doubt, for this substance when heated with zinc-dust was very easily reduced to diphenyl, distinctly recognised by its melting point and odour. We have not yet sufficient for analysis.

That the reaction takes place during the fusion of the potassium monosulphonate, the sulphonic group and the methylene being simultaneously replaced by hydroxyl, seems quite evident; but we are not yet in a position to account for the formation of two trihydroxydiphenyls.

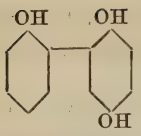
Assuming that the monosulphonate has the SO_3 in the position



the trihydroxy body derived from it would have the constitution



which is probably that of the body melting at 180°, whilst the body of higher melting point (205°) would possibly have the structure



. The former, however, is produced in decidedly larger quantity than the latter. It is, however, possible that two monosulphonic acids are produced by the action of SO_3HCl. These we are trying to isolate.

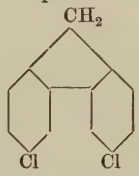
The trioxydiphenyl melting at 180° gives on heating with acetic anhydride an acetate melting at 100°.

As the hydrocarbon itself was so readily acted upon by fused potash, it was thought that the halogen-compounds might likewise be acted upon under the same circumstances, and that in this way some idea of the mechanism of the reaction would be obtained.

It was attempted in the first place to obtain a more highly brominated body than the dibromfluorene, but this we have not succeeded in doing. The dibromo-compound is acted upon very violently by fused potash, and it has not been found possible to separate the products. It is also acted upon by alcoholic potash, as we shall show later, although the contrary is stated by Barbier (*loc. cit.*).

The chlorine derivatives are much more convenient (we can find no account of their being previously prepared) for this purpose.

Fluorene is moderately soluble in cold chloroform, and if chlorine (dry) be passed into this solution, it is rapidly absorbed, with slight elevation of temperature, up to a point at which nearly the whole of the hydrocarbon has formed a dichloro-derivative (hydrogen chloride being given off), which then separates out of the chloroform in crystals.

The dichlorofluorene *α*- 

forms moderately large colourless plates, melting at 128°, and subliming unchanged.

On oxidation with chromic acid, a dichlorodiphenylene ketone corresponding with the bromo-compound is produced. Its tint of yellow is lighter than that of the dibromo-ketone. It melts at 158°, and distils without decomposing.

By acting on the dichlorofluorene dissolved in boiling chloroform, or better in carbon tetrachloride, with chlorine, more highly chlorinated products have been obtained. The highest product obtained in this way, by the aid of a trace of iodine to the CCl_4 solution, appears to be a pentachlordichloride.

Analysis of the perchlorinated compound once crystallised from alcohol, and melting at 104°:—

0·0759 gram substance, heated with lime (Iceland spar) took 27 c.c. Ag solution. 1 c.c. = 0·00168 Cl = 59·8 per cent. Cl.
0·0902 gram substance = 32·5 c.c. Ag solution.

		Found.	
$C_{13}H_3Cl_7$ = Cl 60·6	I.. 59·8	II.. 60·5	

The substance is still not quite pure, the long needle-shaped crystals of the permanently perchlorinated body being accompanied by small cubic crystals of apparently the same solubility in alcohol.

This perchlorinated substance is readily oxidised by chromic acid, giving a yellow ketone (?) melting at 103—104°.

A totally different chlorine-derivative is produced when the gas is passed into boiling fluorene (both quite dry). Hydrogen chloride is then given off, and the boiling point rises from about 300° to over 360°; no decomposition, however, appears to take place, and the resulting chlorinated substance remains liquid or semi-liquid, even at 0°. It is not oxidised by chromic acid. The results of further study of this body will be given later.

Fused potash acts very energetically on the chloro-derivatives, much more so than in the case of the dibromofluorene.

With the body termed provisionally the perchlorinated substance, reaction takes place with almost explosive violence, and compound containing chlorine being volatilised by the heat of the reaction.

Alcoholic potash acts upon the substance ($C_{13}H_5Cl_7$), producing a beautiful red or pink coloration, due to the formation of a body containing less chlorine. This substance is insoluble in alcohol, but dissolves in chloroform, petroleum, and acetic acid, from which solutions it crystallises on slow evaporation. It melts to a deep red liquid at about 110°, and crystallises on cooling. Nitric and chromic acids are without effect upon it. It is a most difficult substance to analyse, as it almost refuses to burn. These analyses are therefore only very approximate.

Red Body containing Chlorine.

I. 0·1328 substance = 40·5 c.c. Ag sol. 1 c.c. = 0·00168 Cl, 51·2 per cent. Cl.

II. 0·0893 substance = 27·25 c.c. Ag sol., 51·2 per cent. Cl.

0·1035 gram substance = 0·1657 CO_2 and 0·0193 OH_2 = C 43·7, H 2·06.

0·0123 gram took 27·3 c.c. Ag sol. = Cl 51·2 per cent.

		Found.
C_{13}.....	46·0	43·7
H_5.....	1·5	2·06
Cl_5	52·5	51·2

We find that a mixture of potassic hydrate and carbonate acts much less energetically than the potash alone, and we hope to be able soon to obtain the haloïd dihydroxydiphenyls by this means.

The α-dibromo-fluorene forms a sulphonic acid which is obtained by the action of sulphuric chlorhydrin in theoretical proportion, on the dibromo-derivative in chloroform solution. On evaporation of the solvent, beautiful colourless crystals of the free acid are obtained. It melts at 142°, and decomposes at a few degrees higher. The barium salt forms colourless crystals.

Analysis.

I.... 0·0765 gram water lost 0·010 at 120°.

II.... 0·2029 gram lost 0·0260 and gave 0·0431 $BaSO_4$. = 0·02534 Ba.

	$(C_{13}H_7Br_2SO_3)_2Ba + 8OH_2$.	Found. I.	Found. II.
OH_2....	13·28	13·08	12·88
Ba	14·52	—	14·32

We are continuing the investigation of these derivatives.

XXIV.—*On α-Ethylvalerolactone, α-Ethyl β-Methylvalerolactone, and on a Remarkable Decomposition of β-Ethyl-aceto-succinic Ether.*

By Sydney Young, B.Sc., Strassburg University.

α-Ethylvalerolactone.

Fittig and Krafft (*Annalen*, **208**, 71) prepared a heptolactone of unknown constitution from teracrylic acid, and examined its properties. At Professor Fittig's suggestion the following work was undertaken to prepare a heptolactone of known constitution so as to compare it with the above-mentioned compound.

To a cooled solution of 10·2 g. of sodium in about 100 g. alcohol, 58 g. acetoacetic ether were added, and 87 g. α-bromobutyric ether then gradually introduced. The mixture was heated on the water-bath until it became neutral, the reaction being complete in about two days. The alcohol was then distilled off and the ether washed with water, dried with calcium chloride, and distilled. The boiling point of β-ethyl-aceto-succinic ether is given by Thorne (*Chem. Soc., J.*, **39**,

336) as 267°, but I did not get a constant boiling point. Portions were collected after two fractionations below 260°, from 250—260°, from 260—265°, and above 265°.

About 12 g. of the portion between 250° and 260° was boiled with twice its weight of hydrochloric acid, 1 part concentrated acid to 2 of water, for about two days, until the oily layer had disappeared. The resulting product, consisting mostly of α-ethyl-β-acetopropionic acid, was then extracted with ether and the latter distilled off.

The residue crystallised in part at the temperature of a mixture of ice and salt. It was therefore left in a desiccator in the ice-chamber for two or three days, after water had been added, and evaporated off to remove the last traces of ether and alcohol. The crystals were collected on a filter, washed with a little cold water, and dried between filter-paper. They were difficultly soluble in cold water, but much more easily in hot, and good crystals were obtained from the aqueous solution.

About 3·5 g. of the filtrate was dissolved in about 200 c.c. of water and treated with 175 g. of 4 per cent. sodium-amalgam. The liquid was cooled at first, but was finally warmed on the water-bath. The reaction was complete in about three days, when the liquid was poured from the mercury, and any impurities extracted with ether. The solution was then acidified with sulphuric acid and boiled for half an hour in a flask with reversed condenser. When cool it was made alkaline with potassium carbonate and extracted with ether. The residue from the ether was dried with potassium carbonate and distilled. The greater part came over between 218° and 220°. The lactone was redistilled, and was found to boil constantly at 219·5° (thermometer entirely in the vapour). It did not solidify in a mixture of snow and salt.

On analysis 0·2556 g. lactone gave 0·6120 CO_2 and 0·2180 H_2O.

C per cent.	= 65·30.	Calc. for $C_7H_{12}O_2$ C per cent.	= 65·62.
H „	= 9·47.	„ „ H „	= 9·37.

The sp. gr. of the lactone at 16° was 0·992.

Some of the lactone was dissolved in the smallest possible quantity of ice-cold water. The liquid was quite clear, but became turbid at about 17°, and remained so up to about 95°, when the lactone was redissolved; on cooling the solution became turbid at about 90° and clear again at from 15—20°. It was quite neutral.

This lactone, therefore, exhibited the peculiar properties possessed by those previously obtained, but it differed from the heptolactone obtained by Fittig and Krafft, which solidified at 0°, its melting point being about 11° (*Annalen*, **208**, 88).

The formation of the compound is expressed thus :—

$$CH_3.CO-CH_2-CH(C_2H_5)-COOH + H_2 = CH_3-CH.OH-CH.C_2H_5-COOH$$

and

$$CH_3-CH(OH).CH_2.CH(C_2H_5).COOH-H_2O = \begin{array}{l} CH_3-\underset{\displaystyle |}{C}H-CH_2-\underset{\displaystyle |}{C}H.C_2H_3 \\ \qquad\; O\text{—————}CO \end{array}$$

Barium α-ethyloxyvalerate, $(CH_3.CH.OH.CH_2.CH.C_2H_5.CO_2)_2Ba$, was prepared by boiling the lactone with barium hydrate about $2\frac{1}{2}$ hours until the former disappeared. The excess of barium was precipitated with carbon dioxide, and the carbonate removed by filtration. The filtrate was evaporated to a syrupy mass, redissolved in water filtered from deposited barium carbonate, and again evaporated to dryness, but more barium carbonate was precipitated. The residue was therefore dissolved in absolute alcohol, filtered, and left in a desiccator over sulphuric acid. A gummy mass was thus obtained which, after a time, assumed a porcelain-like appearance.

A portion was dried till constant at 60°. At 100° it lost weight rapidly with formation of barium carbonate.

On analysis 0·2860 g. barium salt dried at 60° gave 0·1554 $BaSO_4$.

Ba per cent. = 31·95. Calc. for $(C_7H_{13}O_3)_2Ba$ = 32·08.

It was found that the salt obtained by slow evaporation of the alcoholic solution did not dissolve, either in alcohol or water, to a perfectly clear solution, so that the salt is not very stable even at ordinary temperatures.

The *silver salt* was prepared by adding silver nitrate to a concentrated solution of the barium salt. A dense cheesy-white precipitate was thus formed which was easily soluble in both hot and cold water, but much more so in the former. The liquid blackens on boiling, and slowly in the cold. Some of the precipitate was filtered with the pump, pressed between filter-paper, and then dissolved in a little hot water and filtered while hot. The filtrate on cooling deposited part of the salt, more being obtained by passing a current of air over the gently warmed solution in the hot water-bath.

The salt was analysed, when 0·1165 g. gave 0·0495 g. Ag
and 0·0988 „ 0·0425 „

Ag per cent. (1) 42·49. Calc. for $C_7H_{13}O_3Ag$ = 42·69.
„ „ (2) 43·02.

On acidifying the barium or silver salt at 0°, and to a smaller extent at ordinary temperatures, and shaking with ether, a piece of moistened blue litmus-paper dipped in the ether became red, but when the acidified solution was previously boiled the ethereal solution was perfectly neutral.

Again, on precipitating the barium or silver salt with an acid and filtering at once, the addition of potassium carbonate caused the separation of some lactone which was extracted with ether.

Thus at ordinary temperatures a mixture of lactone and oxy-acid is formed, the latter being too unstable to obtain free from lactone.

Decomposition by Heat of β-Ethyl-aceto-succinic Ether.

On preparing larger quantities of the crystalline acid, which will be called *ketolactonic acid*, the portion of β-ethyl-aceto-succinic ether coming over between 260° and 265° was found to yield proportionately a much larger quantity of crystals than that between 250° and 260°, while the distillate above 265° yielded still more. It thus appeared as if the decomposition had taken place during the distillation and not during the saponification. A portion of the liquid coming over above 265° was therefore slowly distilled until about a third had gone over. The distillate was fractionated, when it was found that a considerable portion of it came over below 100°. This distillate was light, limpid, and burned with a clear blue flame, whereas the ether is almost incombustible. It also gave the iodoform reaction with iodine and caustic soda, and was therefore alcohol. It appeared to be formed thus :—

$$C_{12}H_{20}O_5 = C_{10}H_{14}O_4 + C_2H_6O.$$

On saponification, the remaining C_2H_5-group was apparently simply replaced by hydrogen, thus :—

$$C_{10}H_{14}O_4 + H_2O = C_8H_{10}O_4 + C_2H_6O.$$

The ketolactonic acid was found to have the formula $C_8H_{10}O_4$, as above.

The aqueous solution, which was strongly acid, deposited well-formed crystals which were washed with cold water, dried between filter-paper, and then in the air-bath at 60°. The melting point was found to be 181°, but, on repeated fusion and solidification, the melting point was lowered slightly, the acid apparently decomposing to some extent.

Analysis of the acid dried at 100° :—

I. 0·1640 g. acid gave 0·3409 CO_2 and 0·0940 H_2O.
II. 0·2669 „ „ 0·5516 „ 0·1419 „

C per cent.	(1) 56·69	(2) 56·37.	Calc. for $C_8H_{10}O_4$ C per cent.		56·47.
H „	6·37	5·90.	„ „ H „		5·89.

Barium Ketolactonate, $(C_8H_9O_4)_2Ba + 2H_2O$.

A quantity of the acid was dissolved in water and excess of barium carbonate added. The excess of carbonate was filtered off, and the filtrate evaporated to dryness. The residue was dissolved in water, filtered, evaporated to a small bulk, and allowed to crystallise.

The well-formed crystals were pressed between filter-paper, left in the desiccator a short time, and analysed.

0·2814 g. barium salt dried till constant at 100°, lost 0·0154 g. H_2O
" " 130°, " 0·0199 "
" " 130°, gave 0·1278 g. $BaSO_4$.

A second analysis, which will be referred to later, gave the following numbers:—

0·2027 g. lost at 100° 0·0099 g. H_2O, and at 130° 0·013, and gave 0·0925 g. $BaSO_4$.

	Calc. for $(C_8H_9O_4)_2Ba + 2H_2O$.		Found.	
$1\frac{1}{2}H_2O$ =	5·28	(1)	5·47	(2) 4·89
$2H_2O$ =	7·04		7·07	6·41
Ba =	26·81		26·72	26·83

The salt began to decompose above 130°, and the crystals lost water slowly in the desiccator.

When the salt is evaporated nearly to dryness on the water-bath and treated with alcohol, it is obtained as a white anhydrous powder.

On analysis 0·2519 g. salt dried at 100° gave 0·1249 g. $BaSO_4$.
Ba per cent. = 29·15. Calc. for $(C_8H_9O_4)_2Ba$ = 28·84.

The silver salt was obtained by heating a solution of the barium salt with silver nitrate. When deposited from a dilute solution it is distinctly crystalline. It is slightly soluble in water and insoluble in alcohol. The dry salt is scarcely coloured by the light, but the aqueous solution blackens slowly.

On analysis 0·1455 g. silver salt gave on ignition 0·0569 g. Ag.
0·3163 " " combustion 0·4019 g. CO_2, 0·0947 H_2O, and 0·1243 Ag.

C per cent.	(1) —	(2) 34·65	Calc. for $C_8H_9O_4Ag$	34·65
H "	—	3·33	" "	3·25
Ag "	38·90	39·29	" "	38·99

Action of Barium Hydrate on Ketolactonic acid.

On adding barium hydrate to a solution of the acid, the liquid remains clear in the cold, even after long standing, but when it is

heated to nearly 100° a sudden and copious precipitation of barium carbonate takes place.

Some of the acid was treated with excess of barium hydrate and left in the cold for two days, the liquid remaining perfectly clear. The excess of barium was precipitated with carbon dioxide, and the carbonate removed by filtration. The filtrate when warmed deposited barium carbonate rapidly, but the salt was precipitated on addition of alcohol to the aqueous solution. A portion of the filtrate was treated in this way, but the precipitated salt was gelatinous and difficult to filter, and the residue contained a large quantity of barium carbonate. In this condition it was difficultly soluble in water, and the large amount required for solution prevented its reprecipitation by alcohol. The remainder was allowed to stand in an exhausted desiccator, but it deposited barium carbonate slowly. It was therefore filtered and treated with silver nitrate, when a white granular precipitate was obtained, which was less soluble than silver ketolactonate. It was filtered, dried between filter-paper, and placed in the desiccator. It decomposed even at 60°, and the aqueous solution blackened on heating.

The analyses, though not very accurate, showed that this was the salt of a dibasic acid derived from ketolactonic acid.

I. 0·0865 gram silver salt gave 0·0459 Ag.
II. 0·0809 „ „ 0·0428 „
III. 0·1191 „ „ 0·0996 CO_2 and 0·0299 H_2O.

	Calc. for $C_8H_{10}O_5Ag_2$.	Found.		
C per cent.	= 23·88	(1) —	(2) —	(3) 22·81
H „	= 2·49	—	—	2·79
Ag „	= 53·73	53·06	52·90	—

There was not enough substance for a thorough investigation of the acid, but the filtrates from the silver salt were acidified, exhausted with ether, and the latter evaporated. The acid thus formed was mostly liquid, but contained a few crystals, which, when dried between filter-paper and in the desiccator, were found to melt at 181°, and appeared therefore to be ketolactonic acid.

Some of the crystalline acid was boiled for half an hour with barium hydrate. When the temperature approached 100° a sudden precipitation of barium carbonate took place, the action being apparently complete in a very short time. After removal of the excess of barium in the usual way, and evaporation of the filtered solution, the salt was obtained as a gummy mass. It was dissolved in absolute alcohol and left in the desiccator. The salt resembled barium γ-oxy-ethyl valerate in appearance, and could not be crystallised.

0·1470 barium salt dried at 100° gave 0·0815 $BaSO_4$.
0·2200 „ „ „ 0·1217 „

Ba per cent. (1) 32·45. Calc. for $(C_7H_{11}O_3)_2Ba$ = 32·39.
„ „ (2) 32·53.

The reaction may be expressed thus—

$$2C_8H_{10}O_4 + 3BaO + H_2O = 2BaCO_3 + (C_7H_{11}O_3)_2Ba.$$

The silver salt was easily soluble in water, and very unstable, and was not obtained pure. On acidifying it with hydrochloric acid and exhausting with ether, a liquid acid was obtained, but the quantity was too small to allow of investigation.

Ethylsuccinic Acid.

Thorne obtained two acids by the saponification of β-ethylacetosuccinic ether, viz., α-ethyl-β-acetopropionic acid and ethylsuccinic acid.

So far I had obtained the first of these, and also the new ketolactonic acid. Since there was always a certain amount of acid unacted on by sodium-amalgam, it seemed probable that this was ethylsuccinic acid. This residual acid was therefore treated with barium carbonate, and filtered. After evaporation part of the residue was soluble, part insoluble, in alcohol. The insoluble salt was purified by repeatedly dissolving in water, evaporating to a small bulk, and precipitating with alcohol. After repeating this process six times, the salt was obtained almost colourless, but the acid when set free did not crystallise. The barium salt was again prepared, and the purification repeated as far as the small amount of substance permitted.

The percentage of barium (43·37, calc. for $C_6H_8O_4Ba$ = 48·75) was much higher than in either of the other salts, and Thorne describes the salt as being extremely difficult to obtain in a state of purity, so that it was probably impure barium ethylsuccinate.

On α-Ethyl-β-methylvalerolactone.

Methylacetoacetic ether was first prepared by the action of sodium ethylate and methyl iodide on acetoacetic ether, and was employed in place of acetoacetic ether in the preparation of the lactone, just as in the previous case. The yield, however, was very poor, and the lactone contained some of the lower homologue, the action of the sodium ethylate and methyl iodide being apparently incomplete.

A quantity of β-ethylacetosuccinic ether was therefore prepared as before, and a portion was treated, after drying with calcium chloride, but without distillation, with sodium ethylate and methyl iodide, so

as to obtain β-ethylacetomethylsuccinic ether. The latter was then distilled, when it was found that alcohol was again split off, and after saponification a crystalline acid was again obtained. The lactone was prepared as before, but boiled between 219° and 226°, so that the action of sodium ethylate and methyl iodide was again incomplete. The failure of this reaction was also noticed by Mr. Gottstein in this laboratory.

The crystalline acid melted at 181°, and was found on analysis to be ketolactonic acid. The analysis of the hydrated salt $(C_8H_9O_4)_2Ba + 2H_2O$ has been already given.

Of the anhydrous salt 0·1803 g. gave 0·0883 g. $BaSO_4$.
Ba per cent. 28·79. Calc. for $(C_8H_9O_4)_2Ba$ = 28·84.

The remainder of the β-ethylacetosuccinic ether was distilled, and the portions coming over between 257° and 270° treated with sodium ethylate and methyl iodide. This time 1½ times the calculated quantities of sodium and methyl iodide were used, and the ether was dried with potassium carbonate, calcium chloride being partially dissolved by these ethers. The greater part distilled between 260° and 275°. On saponification no crystals were obtained, even from the portion boiling above 275°.

The lactone was obtained as before. The greater part distilled between 224° and 228°, but even after repeated fractionation a constant boiling point was not obtained, though the greater portion of the substance came over between 226° and 227°, and this was therefore analysed.

0·2311 gram lactone gave 0·5677 gram CO_2 and 0·2019 H_2O.
0·1135 „ „ 0·2799 „ 0·1016 „

C per cent. (1) 67·00 (2) 67·26. Calc. for $C_8H_{14}O_2$ C per cent. 67·60.
H „ 9·71 9·94. „ „ H „ 9·86.

The lactone was therefore moderately pure.

An analysis of the portion distilling between 224° and 225° was also made.

0·2124 gram lactone gave 0·5184 CO_2 and 0·1855 H_2O.

C per cent. = 66·56. Calc. for $C_8H_{14}O_2$ = 67·60 and for $C_7H_{12}O_2$ = 65·62.
H „ = 9·70. „ „ = 9·86 „ „ = 9·37.

Since the lactones boil without the slightest decomposition, the residues which remained in the bulbs after the highest fractionations were used to prepare the barium salt.

Barium α-ethyl-β-methylvalerate prepared as above was obtained as a gummy mass exactly resembling the lower homologue. On analysis—

0·2143 gram barium salt dried at 60° gave 0·1094 gram $BaSO_4$.
0·1942 „ „ „ 0·0988 „ „

Ba per cent. (1) 30·02. Calc. for $(C_8H_{15}O_3)_2Ba$ = 30·11.
(2) 29·91.

The barium salt was therefore perfectly pure.

The silver salt resembled that obtained from α-ethylvalerolactone, but was somewhat less soluble in water and rather more stable.

The formation of the lactone is thus expressed:—

$$CH_3.CO.CH.CH_3—CH.C_2H_5—COOH + H_2 = CH_3.CH.OH—CH.CH_3—CH.C_2H_5—COOH$$

and $CH_3.CH.OH—CH.CH_3—CH.C_2H_5—COOH$ =

$$\begin{array}{l} CH_3.CH—CH.CH_3—CH.C_2H_5 \\ \quad\;\; | \qquad\qquad\qquad\quad\;\; | \\ \quad\;\; O\text{———————}CO \end{array}$$

The residual acid, after treatment with sodium-amalgam, was treated just as in the previous case. After repeated purification of the barium salt, the acid was set free, and was found to crystallise. After pressing between filter-paper, the crystals melted between 158° and 160°.

The barium salt was prepared from the crystals, and after drying at 70°—

0·1080 gram yielded 0·0839 $BaSO_4$. Ba per cent. = 45·68.
Calc. for $C_7H_{10}O_4Ba$ = 46·44.

There was not enough substance to allow of further purification, but the analysis shows that ethylmethylsuccinic acid is formed in small quantities by the saponification of β-ethylacetomethylsuccinic ether with hydrochloric acid.

Note on the Anhydride prepared by Thorne (Chem. Soc. J., **39**, 336).

Thorne states that by distillation of α-ethyl-β-acetopropionic acid, an anhydride is formed, and he examined the properties of this compound to some extent. Having a mixture of the two homologous substituted propionic acids mentioned in this paper, which was otherwise useless, I repeated Thorne's experiments, obtaining a similar anhydride, or rather mixture of anhydrides, which boiled at about the same temperature as the corresponding lactones. Thorne states that the anhydride is insoluble in water, but I found, on the contrary, that the mixed anhydrides were slightly soluble, and distinctly more so at about 0° and 100° than at intermediate temperatures, thus resembling the saturated lactones in this peculiar property.

Constitution of Ketolactonic Acid.

It has been seen that this acid is formed from the compound

$$\begin{array}{l} COOC_2H_5 \\ | \\ CH.CO.CH_3 \\ | \\ CH.C_2H_5 \\ | \\ COOC_2H_5 \end{array}$$

, and not from its homologue,

$$\begin{array}{l} COOC_2H_5 \\ | \\ C(CH_3.).CO.CH_3 \\ | \\ CH.C_2H_5 \\ | \\ COOC_2H_5 \end{array}$$

, and that in the former case alcohol is split off.

One of the $(O.C_2H_5)$ groups and an additional H-atom must then be removed from the first compound to form the alcohol. As regards the hydrogen-atom, the only difference between the two ethers is that an H-atom in the one is replaced by CH_3 in the other; but in the latter case no crystalline acid is formed. It is therefore at least probable that this hydrogen-atom is the one removed. It is also almost certain that it is the (OC_2H_5) group farthest from this H-atom which is split off, because if so an unsaturated lactone group would be formed thus—

$$\begin{array}{l} CH_3—CO \quad COOC_2H_5 \\ \quad\quad | \quad\quad | \\ \quad\quad CH—CH \\ \quad\quad | \quad\quad | \\ C_2H_5OCO \quad C_2H_5 \end{array} = \begin{array}{l} CH_3C—O—CO \\ \quad\quad \| \quad\quad | \\ \quad\quad C———CH \\ \quad\quad | \quad\quad | \\ C_2H_5OCO \quad C_2H_5 \end{array} + C_2H_5OH,$$

and the acid appears in its behaviour with the carbonate and hydrate of barium to contain such a group.

Moreover the splitting off of alcohol in this way would resemble the formation of an unsaturated anhydride noticed by Thorne on distillation of α-ethyl-β-acetopropionic acid, which anhydride (or at least its next homologue) resembles the lactones markedly in its solubility in water.

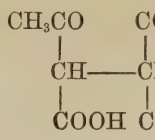
Ketolactonic acid would then be obtained from its ether by simple saponification.

The barium salts, or for the sake of clearness the acids derived from ketolactonic ether, would then be—

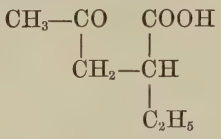
(1.) Ketolactonic acid yielding a barium salt when treated with barium carbonate—

$$\begin{array}{l} CH_3—C—O—CO \\ \quad\quad\quad \| \quad\quad | \\ \quad\quad\quad C———CH \\ \quad\quad\quad | \quad\quad | \\ \quad\quad\quad COOH \; C_2H_5 \end{array}$$

(2.) Probably β-ethylacetosuccinic acid, obtained by the action of barium hydrate in the cold, that is by simple addition of H_2O—



(3.) Probably α-ethyl-β-acetopropionic acid by the action of barium hydrate at 100°, that is by removal of CO_2 from the last acid—



Since ketolactonic acid is decomposed by boiling with barium hydrate, it is easy to understand why Thorne did not obtain it, since he saponified the ether by boiling with caustic potash, so that the acid would be decomposed as soon as formed.

Before closing this paper I wish to return my sincere thanks to Professor Fittig for his ever ready advice and assistance in carrying out this investigation.

XXV.—*On the Constitution of Molecular Compounds. The Molecular Weight of Basic Ferric Sulphate.*

By Spencer Umfreville Pickering, B.A. Oxon, Lecturer in Chemistry at Bedford College.

In representing basic compounds, two methods of notation are commonly adopted: the one consists in representing the compound as a combination of molecules of the metallic oxide with molecules of the non-metallic oxide, as, for instance, $4CuO,SO_3$; the other, in representing it as a combination of molecules of the metallic oxide with the normal sulphate; thus, $CuSO_4,3CuO$. In using this latter form we hint at an analogy between a basic salt and a hydrated salt, the metallic oxide in the former occupying a position similar to that which the water does in the latter.

Taking, now, the only known basic ferric sulphate, we may represent it either as $2Fe_2O_3,SO_3$, or as $Fe_2(SO_4)_3,5Fe_2O_3$; the former indicating its molecular weight to be 400, the latter indicating it to be 1200; if, therefore, a determination of the weight of its molecule showed it to be 400, it would render the latter method of representation impossible.

The only means of determining the molecular weight of a stable

solid, such as basic ferric sulphate, which promised any success, was in ascertaining, if possible, the unit of water removable from a hydrated specimen of it.

In 1879 the author performed a few experiments on basic ferric sulphate, which indicated that definite hydrates were formed, not only by exposing this substance to dry air at various temperatures, but also by exposing it to air saturated with moisture; the results of these preliminary experiments were communicated to the Ashmolean Society of Oxford, February, 1880. Somewhat similar experiments on certain metallic oxides were performed by C. F. Cross (*Chem. Soc. J.*, Trans., 1879, 796), who showed that definite hydrates of oxides were obtainable by the action of moist air on them, and also that the hydrates thus obtained in any particular case depended on the temperature to which the oxide had previously been exposed. It will be seen below that similar results are obtained with basic salts.

Two samples of basic ferric sulphate were prepared by the action of a defecit of sodic carbonate on the normal sulphate (see this Journal, Trans., 1880, 807), and dried by exposure to air, without the application of heat. The first sample was used in experiments A and B, the second in experiments C and D.

A glass boat, containing a portion of the basic salt, was placed in a tube passing through a water-bath, and through this tube a current of thoroughly dried air was drawn by means of a water-pump.

In no case was the sulphate found to contain the least trace of carbonate; nor was it found to give off any traces of sulphuric acid (tested in experiment C, which lasted for 44 days).

The exposure to moist air was effected in the earlier experiments by passing a very slow current of moist air over the sulphate, and, in the latter experiments, by leaving the sulphate under a bell-jar in presence of a dish containing water, the whole being placed in a cellar where the temperature was constant. The temperatures mentioned below are the highest reached during the heating in any particular case.

The letters given in the first column of the accompanying table refer to the experiments, and the numbers, to the order of the various operations in each. In experiment A the weight of anhydrous substance taken (as determined by subsequent analysis) was 0·4264 gram, and H_2O would therefore correspond to 0·0064 gram, taking the triple formula: in B 2·0806 grams taken, $H_2O = 0·312$ gram; in C 0·8163 gram taken, $H_2O = 0·01224$ gram; and in D 0·81604 gram taken, $H_2O = 0·012237$ gram. In the last two experiments the current of air was much slower than in the first two.

That the constant weights attained by the basic salt correspond to definite hydrates there can be little doubt. Altogether 28 constant

Exp.	Hydrate obtained.	Conditions under which obtained.	Time during which		Molecular weight.		
			It lost or gained weight.	It remained constant.	Found.	Calc.†	Diff.
A (7)	$Fe_2(SO_4)_3,5Fe_2O_3,8H_2O$	In dry air at 100° C.	12 hours	—	1341·34	1341·34	0
C (2)	,,	,, at ,,	12 days	8 days	1341·44	,,	+0·10
A (9)	$Fe_2(SO_4)_3,5Fe_2O_3,11H_2O$	,, at 17° C. after being heated at 100° C.	26 hours	—	1394·66	1395·22	−0·56
A (10)	,,	,, at ,, ,, ditto and moistened ..	—	—	1396·06	,,	+0·84
B (12)	,,	,, at 93° C.	7 days	1 day	1396·66	,,	+1·44
A (3)	$Fe_2(SO_4)_3,5Fe_2O_3,12H_2O$	,, at 72° C.	—	—	1412·90	1413·18	−0·28
A (5)	,,	,, at 85° C.	—	—	1412·90	,,	−0·28
A (8)	,,	moist at 17° C. after being heated at 100° C.	22 hours	—	1413·74	,,	+0·56
B (11)	,,	dry at 85° C.	2 days	2 days	1413·36	,,	+0·18
D (4)	,,	,, at 57° C.	50 ,,	6 ,,	1412·91	,,	−0·27
B (10)	$Fe_2(SO_4)_3,5Fe_2O_3,13H_2O$	,, at 74° C.	5 ,,	1 day	1429·10	1431·14	−2·04
B (9)	$Fe_2(SO_4)_3,5Fe_2O_3,14H_2O$	,, at 63° C.	8 ,,	—	1449·46	1449·10	+0·36
B (8)	$Fe_2(SO_4)_3,5Fe_2O_3,15H_2O$	,, at 52° C.	2 ,,	1 ,,	1467·18*	1467 06	+0·12
D (1)	,,	,, at 16° C.	10 ,,	3 days	1469·44	,,	+2·38
A (1)	$Fe_2(SO_4)_3,5Fe_2O_3,16H_2O$	,, at 18° C.	—	—	1484·46	1485·02	−0·56
A (6)	,,	moist at 18° C. after being heated at 85° C.	70 hours	—	1485·86	,,	+0·84
B (1)	,,	dry at 17—23° C.	35 days	—	1485·32	,,	−0·13
B (5)	,,	,, at ,, after exposure to moist air	38 ,,	1 day	1486·82*	,,	−1·80
B (7)	,,	,, at 38° C.	4 ,,	—	1485·02*	,,	0
C (1)	,,	,, at 35° C.	20 ,,	4 days	1485·34	,,	+0·32
A (4)	$Fe_2(SO_4)_3,5Fe_2O_3,17H_2O$	moist at 17° C. after being heated at 72° C.	—	—	1502·70	1502·98	−0·28
A (2)	$Fe_2(SO_4)_3,5Fe_2O_3,26H_2O$	,, at 18° C. before being heated at all ..	—	—	1665·46	1664·62	+0·84
D (2)	$Fe_2(SO_4)_3,5Fe_2O_3,36H_2O$	,, at 13—18° C.	77 ,,	4 ,,	1845·33	1844·22	+1·11
D (3)	$Fe_2(SO_4)_3,5Fe_2O_3,37H_2O$	,, at 7—12·7° C.	46 ,,	99 ,,	1863·47	1862·18	+1·29
B (3)	$Fe_2(SO_4)_3,5Fe_2O_3,38H_2O$	,, at 14·2° C.	6 ,,	1 day	1880·68	1880·14	−0·54
B (4)	$Fe_2(SO_4)_3,5Fe_2O_3,39H_2O$	,, at 13·2° C.	1 day	5 days	1898·46	1898·10	−0·36
B (6)	,,	,, at 10° C. after being heated at 38° C.	66 days	several ,,	1898·46	,,	−0·36
B (2)	$Fe_2(SO_4)_3,5Fe_2O_3,40H_2O$	,, at 12° C. before being heated at all ..	64 ,,	—	1916·42	1916·10	−0·42

* Not very reliable.

† O = 15·96, S = 31·98, Fe = 55·9. $Fe_2(SO_3)_4,5Fe_2O_3$ = 1197·66.

weighings were obtained, and all of these correspond to the theoretical numbers within the limits of probable error, the greatest difference between the observed and calculated weights being only + 0·16 per cent., and the average differences being + 0·04 and — 0·03 per cent. of the total weights.

Now of the 14 different hydrates thus obtained, four only can be represented by the simpler formula $2Fe_2O_3,SO_3,xH_2O$, while the remaining 10 necessitate the adoption of the triple formula

$$Fe_2(SO_4)_3,5Fe_2O_3,yH_2O.$$

Even had there been obtained but one hydrate of this latter class, it would, in my opinion, have shown that the empirical molecular weight must be trebled; but the existence of so large a number of them must put the question beyond all doubt.

These experiments prove with almost equal certainty that no more complex formula than the triple one is required: for between the extreme hydrates actually obtained, 33 different hydrates are possible if the molecular weight be 1200 (corresponding to the triple formula), and if the molecular weight were double, namely, 2400, 66 hydrates would be possible. Now of these possible hydrates 14 have been obtained, all of which correspond to the molecular weight 1200, and not to 2400. The odds, therefore, in favour of the true weight being 1200 will be found to be about 95,000 : 1; and, making allowance for the fact that many of these hydrates were obtained several times, these odds will be increased to as much as 14,400,000,000,000 : 1; in other words, it is practically a certainty that the molecular weight of basic ferric sulphate is 1200, and that it may therefore be represented by the formula $Fe_2(SO_4)_3,5Fe_2O_3,xH_2O$, but not by any simpler or more complex formula.

XXVI.—*The Phenates of Amido-bases.*

By R. S. Dale, B.A., and C. Schorlemmer, F.R.S.

Our hope to get hold of the intermediate compounds supposed to be capable of existing between aurin and pararosaniline, has not yet been fulfilled (this Journal, 1879 [i], 148). A long series of experiments has convinced us that, on heating aurin with aqueous or alcoholic ammonia, the action proceeds at once to the formation of pararosaniline, which can easily be detected, even if only a trace has been formed, by dissolving the product in a little ammonia, adding hot water, and dipping some silk into the liquid. It will soon be dyed magenta-red, as aurin does not dye in an alkaline solution. "Red

aurin" or "peonine" is therefore nothing but aurin containing more or less pararosaniline.

As already stated (this Journal, 1879 [i], 562), methylamine acts more readily on aurin than ammonia, only trimethylpararosaniline being formed, and no intermediate products, which is shown by dyeing silk in an ammoniacal solution, the characteristic shade of Hofman's violet being produced, while the product containing aurin dyes in a neutral or faintly acid solution, a claret colour.

The most remarkable fact is that it is the most difficult to separate the bases from the aurin by means of dilute acids, from which we came to the conclusion that they formed with it definite compounds.

We heated, therefore, equal molecules of aurin and common rosaniline with alcohol. They soon dissolved, and on concentration a crystalline powder having a dark green metallic lustre separated out, which, by recrystallising from hot dilute alcohol, is obtained in well defined crystals.

Rosaniline aurinate is more freely soluble in alcohol than its constituents. It dyes silks exactly like other rosaniline salts, the colour of aurin not interfering. That the compounds go on the fibre as a whole, is shown by the fact that the dye-baths may be completely exhausted without obtaining any other shade.

Aurin being a phenol and rosaniline an amido-base, we tried next to obtain a compound of the two most simple members of both groups, and heated a mixture of equal molecules of aniline and phenol for some hours to the boiling point. After cooling and standing for some time, large thin plates crystallised out, and finally the whole solidified.

Aniline phenate, C_6H_7N,C_6H_6O, forms also slowly in the cold; it crystallises from alcohol or petroleum-naphtha in beautiful glistening plates, melting at 29·5°. Its uncorrected boiling point is 184·5°, and its smell resembles that of phenol, but is much fainter. As it has no irritating action on the skin, and is undoubtedly a powerful antiseptic, it may in many case be advantageously used in place of phenols.

Since these observations were made, we have found that Hofmann's statement (*Annalen*, **74**, 126) as to phenol not acting on aniline, even at 250°, is incorrect. His endeavour was to obtain diphenylamine. The reason why he did not observe the formation of aniline phenate, we cannot explain.

The further investigation of these and other compounds of phenols with amido-bases has been undertaken by Mr. G. Dyson, who, as a mean of three analyses, found in aniline phenate 7·57 per cent. of nitrogen, the calculated percentage being 7·49. He has also already prepared *rosaniline phenate*.

We have already stated that the red alkaline solutions of aurin sometimes turn brown. This change takes place sometimes quickly,

sometimes very slowly; presence of air is not required as we formerly supposed (this Journal, 1879 [i], 562). On adding an acid to the brown solution, a smeary mass is precipitated, from which we could isolate a body forming colourless crystals. This compound is *dioxyphenolketone*, $CO(C_6H_4.OH)_2$, which Cars and Graebe obtained by heating aurin with water to 220—250° (*Ber.*, **11**, 1348).

XXVII.—*On some Derivatives of Diphenylene Ketone Oxide.*

By A. G. Perkin.

The diphenylene ketone oxide employed in the following experiments was prepared by the process recently described by my Father (page 35 of this volume), namely, by distilling a mixture of salicylic acid and acetic anhydride. On concentrating the alcoholic mother-liquors left from the purification of this body, they were found to contain small quantities of a second product. It was afterwards observed that when the mixture of salicylic acid and acetic anhydride was very rapidly distilled, the amount of the new compound produced was larger than when the operation was conducted slowly. At first it was separated from the diphenylene ketone oxide simply by repeated fractional crystallisation, but afterwards the crude diphenylene ketone oxide was macerated with a small quantity of cold alcohol, and, after filtration, the alcohol was removed from the filtrate by boiling with water. Caustic potash was then added to dissolve oily matter present, and the whole was allowed to stand for about an hour, after which the solid matter in suspension was thrown on a filter and well washed. The product thus obtained was crystallised from alcohol, the first crop of crystals separating out being collected apart. By repeated treatment in this way, the new product was obtained in long thin transparent plates, having a beautiful satiny lustre. On analysis, it gave the following numbers:—

I. 0·1391 gram substance gave 0·3870 of CO_2 and 0·0497 of OH_2.
II. 0·1319 „ „ 0·3646 „ 0·0478 „
III. 0·1044 „ „ 0·2861 „ 0·0353 „

These numbers give the following percentages agreeing with the formula $C_{14}H_8O_3$:—

	Calculated.	Found. I.	II.	III.
Carbon	75·0	75·16	75·38	74·74
Hydrogen ..	3·57	3·89	4·02	3·75

This substance is only slightly soluble in boiling alcohol, but more so in coal-tar naphtha. It melts at 192°, and distils with partial decomposition. When boiled with alcoholic potash, it is converted into the potassium salt of an acid, and on adding water and boiling off the alcohol, the acid is precipitated by hydrochloric acid as a somewhat gelatinous product if the solution is cold, but as a bulky precipitate on boiling.

This acid may be purified by two or three crystallisations from alcohol, from which it separates in minute needles. Specimens dried at 100° gave on analysis the following numbers :—

I. 0·1265 gram of substance gave 0·3246 of CO_2 and 0·0431 of OH_2.
II. 0·097 gram of substance gave 0·2488 of CO_2 and 0·0328 of OH_2.
III. 0·1345 „ „ 0·3457 „ „ 0·0416 „
IV. 0·1496 „ „ 0·3838 „ „ 0·0452 „

These give percentages agreeing with the formula $C_{14}H_8O_4$—

		Found.			
	Calculated.	I.	II.	III.	IV.
Carbon.....	70·0	69·98	69·95	70·1	69·98
Hydrogen....	3·33	3·78	3·76	3·44	3·35

This acid melts at 275°. It sublimes in brilliant needles, and can be distilled apparently with but little decomposition; it is difficultly soluble in alcohol. When gently fused with caustic alkali, it produces salicylic acid, judging from the iron reaction.

Silver Salt.—This was prepared by dissolving the acid in dilute ammonia and boiling the solution until it was free from excess of that substance. Silver nitrate was then added by small quantities at a time, the mixture being well agitated. After some quantity of precipitate had been formed, the solution was filtered and an excess of silver nitrate added, which caused the liquid to coagulate into a gelatinous mass, somewhat like precipitated alumina, but, contracting, and becoming crystalline when heated in a water-bath ; it was then collected and well washed with cold water. It gave on analysis the following numbers, the different preparations being examined :—

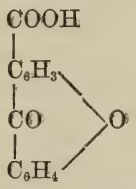
I. 0·1172 gram of substance gave 0·0360 gram Ag.
II. 0·1483 gram of substance gave 0·2642 gram CO_2 and 0·0275 gram OH_2.
III. 0·1881 gram of substance gave 0·0582 gram Ag.

These give percentages agreeing with the formula $C_{14}H_7AgO_4$—

	Calculated.	Found. I.	II.	III.
Carbon.....	48·41	—	48·59	—
Hydrogen ..	2·01	—	2·06	—
Silver	31·1	30·71	—	30·94

This salt is slightly soluble in cold water, more easily in boiling water. From its hot aqueous solution, it is deposited in groups of small transparent needles, which appear very definite under the microscope. It is not coloured by boiling with water.

From the foregoing results, it appears that this acid has the formula $C_{14}H_8O_4$. Its constitution may perhaps be represented thus:—



Its formation from the compound $C_{14}H_8O_3$ is, however, difficult to understand, because if it be an anhydride of the acid, as its properties would indicate, its formula should be $C_{14}H_6O_3$; but this would require 75·6 per cent. carbon and 2·7 of hydrogen. Unfortunately, this matter cannot at present be further investigated, owing to the want of product, which is obtainable from salicylic acid only in small quantities, and then is difficult to purify. I hope, however, to return to this subject.

On the Action of Nitric Acid on Diphenylene Ketone Oxide.

When diphenylene ketone oxide was added to a cold mixture of one part of nitric acid (sp. gr. 1·45) and one part of sulphuric acid, in small quantities at a time, and with constant stirring, it gradually dissolved without evolution of nitrous fumes. As the solution became more and more concentrated, crystals began to separate out, and the operation was continued until the whole had a semi-solid appearance.

The resulting mass was then thrown into a funnel provided with an asbestos plug, and the residue left after the acid had drained off, was washed, first with a little nitric acid (sp. gr. 1·45), then with weaker nitric acid, and finally with water, and dried. The mother-liquor and washings, after standing for some hours, deposited a further crop of these crystals, which were treated in a similar manner.

The product, which consisted of a mass of fine needles having a satiny lustre, was then further purified by crystallisation from alcohol or coal-tar naphtha. On analysis, it gave the following numbers:—

I. 0·1600 gram of substance gave 0·3200 gram of CO_2 and 0·0301 gram of OH_2.

II. 0·1544 gram of substance gave 0·3103 gram of CO_2 and 0·0300 gram of OH_2.

These numbers agree with those required by the formula $C_{13}H_6(NO_2)_2O_2$; thus:—

	Theory for $C_{13}H_6(NO_2)_2O_2$.	I.	II.
Carbon.....	54·54	54·54	54·80
Hydrogen....	2·09	2·09	2·15

Dinitrodiphenylene ketone oxide is very slightly soluble in boiling alcohol, from which it separates on cooling in the form of fine needles, having a beautiful satiny lustre and electrical properties, and which, when viewed under the microscope, affect polarised light. It is more soluble in boiling coal-tar naphtha, and, when heated it sublimes in the form of needles. It melts at 262°.

The acid mother-liquors and washings obtained during the preparation and subsequent purification of dinitrodiphenylene ketone oxide were found to contain a small quantity of a much more soluble compound, which is probably a "mononitro" derivative, but which, up to the present, has not been obtained in a sufficiently pure state to be examined.

Fuming nitric acid (sp. gr. 1·54), well cooled with ice, was found to act on diphenylene ketone oxide in a similar manner to a mixture of nitric and sulphuric acids, but the yield of dinitro-product was not so good, there being produced at the same time a much larger quantity of the more soluble body above referred to.

The Action of Reducing Agents on Dinitrodiphenylene Ketone Oxide.

When dinitrodiphenylene ketone oxide was suspended in alcohol, and digested with tin and hydrochloric acid, it gradually dissolved, and the solution acquired a slightly yellow tint. When the reduction was completed, which was after the lapse of three or four hours, a little water was added and the alcohol boiled off. The solution was then poured into an evaporating dish and set aside to cool. While cooling, it deposited a quantity of semi-crystalline matter, which evidently consisted of the hydrochloride of a new base. This was thrown on a filter, and washed two or three times with dilute hydrochloric acid.

The mother-liquors and washings, when further evaporated, deposited on cooling another crop of crystals, which were treated in a similar manner.

The product was then dissolved in boiling water, filtered, and caustic soda added to the solution. The orange-coloured precipitate thus formed was thrown on a filter, thoroughly washed with water, and dried, after which it was further purified by crystallisation from boiling coal-tar naphtha, from which it separated in the form of orange-coloured needles.

On analysis, the following numbers were obtained :—

I. 0·1129 gram of substance gave 0·2850 gram of CO_2 and 0·0466 gram of OH_2.

II. 0·1149 gram of substance gave 0·2912 gram of CO_2 and 0·0471 gram of OH_2.

These numbers agree with those required by the formula $C_{13}H_6(NH_2)_2O_2$.

	Theory for $C_{13}H_6(NH_2)_2O_2$.	I.	II.
Carbon.....	69·02	68·87	69·11
Hydrogen....	4·42	4·58	4·54

It is therefore *diamidodiphenylene ketone oxide*. This substance when crystallised from coal-tar naphtha appears under the microscope as orange-coloured flat needles, which affect polarised light. It is moderately soluble in boiling coal-tar naphtha, very slightly soluble in boiling water: from the latter it separates out on cooling in the form of long needles. Its best crystallising agent is a mixture of equal parts of alcohol and water, which deposits it in ruby-coloured prismatic needles.

This base forms an acid and a neutral hydrochloride, the former being thrown down on the addition of concentrated hydrochloric acid to a solution of the latter salt.

When an aqueous solution of the dihydrochloride mixed with its own bulk of alcohol was treated with a solution of platinic chloride, a crystalline mass was precipitated, which when examined under the microscope was seen to consist of fine transparent needles, having a pale-yellow colour. These were then thrown on a filter, washed with hydrochloric acid, and dried *in vacuo*.

The analysis of this salt did not yield numbers quite so good as could be wished, owing to its containing small quantities of that derived from the monohydrochloride. They, however, clearly showed that it has the formula $[C_{13}H_6(NH_2)_2O_2.2HCl].PtCl_4$.

This salt is decomposed when treated with alcohol or water, becoming opaque and darker in colour, yielding the platinum salt of the monohydrochloride of the base.

This salt can also be obtained by addition of platinum chloride to a solution of the latter body. It forms reddish-brown needles.

On ignition the following amounts of platinum were obtained:—

I. 0·1468 gram of substance gave 0·0313 gram of platinum.
II. 0·1129 „ „ 0·0242 „
III. 0·3876 „ „ 0·0835 „

These numbers give percentages agreeing with those required for the formula $2[C_{13}H_6(NH_2)_2O_2.HCl].PtCl_4$.

	Theory.	I.	II.	III.
Platinum....	21·10	21·32	21·43	21·54

Both salts are slightly decomposed at 100° C.

The Action of Sulphuric Acid on Diphenylene Ketone Oxide.

Diphenylene ketone oxide dissolves slowly in cold Nordhausen or ordinary sulphuric acid, forming yellow solutions possessing a bluish fluorescence, but which on treatment with water precipitate the original body unchanged.

With the intention of forming a sulpho-acid, diphenylene ketone oxide was dissolved in a small quantity of Nordhausen sulphuric acid, and the solution gradually heated until it no longer gave a precipitate with water. It was then diluted with water, and the solution neutralised with excess of barium carbonate. More water was then added, and the mixture boiled for some minutes and filtered.

The precipitate on the filter was re-exhausted once or twice with boiling water, and after filtration the combined filtrates were evaporated to dryness on the water-bath. The residue was then dissolved in boiling water and filtered; in the course of a few hours the solution became nearly solid owing to the formation of a mass of minute white crystals; these were pressed in a linen filter, recrystallised, and finally dried at 160—180.°

On analysis the following numbers were obtained. It was dried at 160—170°.

I. 0·1333 gram of substance gave 0·1540 gram of CO_2 and 0·0198 gram of OH_2.
II. 0·1212 gram of substance gave 0·1401 gram of CO_2 and 0·0165 gram of OH_2.
III. 0·1786 gram of substance gave 0·0846 gram of $BaSO_4$.
IV. 0·1333 „ „ 0·0635 „

These numbers give percentages agreeing with those required by the formula $C_{13}H_6O_2Ba(SO_3)_2$.

	Theory for $C_{13}H_6O_2Ba(SO_3)_2$.	I	II.	III.	IV.
Carbon	31·77	31·51	31·53	—	—
Hydrogen ..	1·22	1·65	1·51	—	—
Barium	27·90	—	—	27·89	28·00

Barium diphenylene ketone oxide disulphonate is moderately soluble in boiling water, from which it separates out on cooling in the form of small colourless needles which, when viewed under the microscope, do not affect polarised light.

It is a remarkably stable salt, not being decomposed by a temperature of 200°. When crystallised from water, it was found to contain water of crystallisation, which was only expelled by prolonged heating to 160°.

The following determination was made of the water in this salt. A specimen dried in a vacuum when heated to 100°, lost scarcely any weight.

1·3897 dried at 100°, when heated up to 195°, lost 0·0421 OH_2 = 3·29. Theory for one molecule of water = 3·53 per cent.

The free acid was prepared by adding sufficient sulphuric acid to a solution of the foregoing salt to exactly precipitate all the barium, filtering and concentrating the solution on the water-bath, and afterwards further evaporating over sulphuric acid. In this way it was obtained crystallising in minute needles. It is easily soluble in water, and its solution has a rough bitter acid taste. Its aqueous solution gives with barium chloride a precipitate of the barium salt. Solutions of calcium and strontium chloride are not precipitated with it. When fused with caustic alkali the mixture becomes pale-yellow. The resulting products have not yet been examined.

The Action of Bromine on Diphenylene Ketone Oxide.

Diphenylene ketone oxide was heated in a sealed tube with bromine to 180°, the proportion of each used being those requisite for the formation of a "dibromo" compound. After the expiration of about three hours, the contents of the tube were found to be nearly colourless, and as soon as it was opened quantities of hydrobromic acid escaped.

The contents of the tube were then dissolved in boiling alcohol, and on leaving this solution to cool, it was found that the principal portion separated out quickly in the form of long needles.

These were then filtered off and recrystallised two or three times. F. p. = 212·5—213·5.°

On analysis the product gave the following numbers:—

I. 0·1274 gram of substance gave 0·2051 gram of CO_2 and 0·0233 gram of OH_2.

II. 0·1919 gram of substance gave 0·3122 gram of CO_2 and 0·0350 gram of OH_2.

These numbers give percentages agreeing with those required by the formula $C_{13}H_6(Br)_2O_2$.

	Theory for $C_{13}H_6(Br)_2O_2$.	I.	II.
Carbon	44·06	43·93	44·36
Hydrogen....	1·70	2·03	2·02

It is therefore *dibromodiphenylene ketone oxide.*

It was afterwards observed that this body combined with bromine at the ordinary temperature, when exposed to its vapour or otherwise, only a comparatively small quantity of hydrobromic acid being produced. As it appeared that an addition-product was probably formed, weighed quantities were exposed to the action of bromine vapour, then kept over caustic potash, and finally heated to 100°; as no change appeared to take place at this temperature. The following results were obtained:—

I. 0·4605 gram of substance absorbed 0·4357 gram bromine.

II. 0·6536 „ „ „ 0·5945 „

These quantities are rather more than those required to form an addition-product. A quantity of the product obtained in this way was crystallised three times from benzene and then from alcohol, and on analysis gave the following numbers:—

0·1292 gram of substance gave 0·2094 gram of CO_2 and 0·0204 gram of H_2O.

These give 44·2 per cent. carbon and 1·76 of hydrogen. It was in fact dibromodiphenylene ketone oxide. It does not, however, appear to be the only body produced in the reaction, and it is thought that, as so little hydrobromic acid is liberated in its formation, it may be taken up as it is produced by part of the ketone to form another product. It is curious that bromine dissolved in carbon disulphide does not act or acts but slowly on this body.

Dibromodiphenylene ketone oxide crystallises from alcohol, in which it is difficultly soluble, in the form of long thin transparent needles. It is moderately soluble in boiling glacial acetic acid, and is easily soluble in coal-tar naphtha and low-boiling petroleum. It melts at 210° C., and when heated a little above this point sublimes as long rod-shaped needles. Cold concentrated sulphuric acid dissolves it, forming a yellow solution which is devoid of fluorescence. It is not decomposed by boiling with alcoholic potash.

XXVIII.—*Chemico-Microscopical Researches on the Cell-contents of certain Plants.*

By A. B. Griffiths, F.C.S., Member of the Liverpool Association of Science and Arts, Medallist in Chemistry and Botany, &c.

This contribution is a continuation of a paper entitled "Researches on the Growth of Plants under Special Conditions," published in the *Chemical News*, volume 47, page 27. In that paper I stated on experimental grounds that a certain amount of iron in a soluble condition given to a growing plant, rendered it healthier than it would have been if not so treated. I am still continuing these investigations on a large number of different plants, to ascertain if possible whether this is a law of nature, or applicable in special cases only.

Referring to my already published paper on the subject, of the plant (Savoy cabbage) No. I (grown in a soil without a salt of iron being added), the stalk reduced to ashes yielded on analysis 1·502 per cent. of ferric oxide, while the leaves yielded 8·323 per cent. of ferric oxide. Cabbages Nos. II and III (grown in a soil containing ferrous sulphate) yielded the following results:—

	Plant No. II.		Plant No. III.	
	Stalks.	Leaves.	Stalks.	Leaves.
Fe_2O_3	3·521	12·290	3·005	11·832

From these analyses (which were conducted with the utmost care) it will be seen that the plants (Nos. II and III) grown in a soil containing added ferrous sulphate yielded a large percentage of Fe_2O_3 when reduced to ash, and were healthier plants (weighing respectively 9 lbs. 3 oz. and 8 lbs. 6 ozs.) than the plant No. I grown in a soil not containing the added ferrous sulphate, which weighed only 4 lbs. $2\frac{1}{2}$ ozs.

Now comes the question: In what form does this comparatively large percentage of iron exist in the tissues, &c., of the plant? In this communication to the Chemical Society I wish to detail some further experimental researches I have made on the leaves of these plants, which may answer the above question. In passing, I may mention that I am growing various plants in soils containing known quantities of ferrous sulphate, and in due time shall admit them to an experimental inquiry.

Microscopical sections of parts of the fresh leaves of plants Nos. II and III were made and examined with the utmost care. This examination showed that in the protoplasm of the cells containing the chloro-

phyll corpuscles, there were minute crystals. These at first I thought were crystalloïds, but the action of a dilute solution of potassium hydrate caused no swelling up, thus proving that these bodies were true crystals.

These crystals in some parts of the protoplasm were solitary, and in others arranged in groups round a common centre. When potassium ferricyanide was drawn in (by using blotting-paper) between the slide containing the section of the leaf and the cover-slip covering it, these crystals were stained blue, the deepest blue colour being in close proximity to the crystals. This shows that these bodies were crystals of some iron compound. On drawing in barium chloride in a similar manner to that of potassium ferricyanide, a cloudiness appeared in the parts near the crystals, arising undoubtedly from the formation of barium sulphate. I think that, therefore, the right way of interpreting these observations is that the crystals contained in the protoplasm of the cells were crystals of ferrous sulphate. In Dr. Prantl's *Lehrbuch der Botanik*, Luerssen's *Grundzüge der Botanik*, and Professor Sachs' classic work on Botany, it is stated that crystals of calcium carbonate, calcium phosphate, and calcium oxalate, occur in the cells and cell-walls of certain plants; this is a fact well known to scientific men, but I am not aware that crystals of iron compounds have ever been found in the cell-contents of plants before.

From these researches it is evident that the protoplasm of the cells containing the chlorophyll granules contained crystals of ferrous sulphate. Besides, one could see that these microscopic crystals belonged to the monoclinic system, thus giving further evidence of their being $FeSO_4 + 7H_2O$

These crystals were also found in the plant (cabbage) No. I grown without the iron manure; but where there was one cell containing crystals in such plant, ten or twelve cells containing crystals existed in the plants grown in the iron-manured soil. Of course the iron must have been taken up in solution by the roots of the plants, and have ascended through the stems, and so reached the cells of the leaves; and it may be probable that as transpiration goes on, the solution (cell-sap) becomes saturated, and crystals of ferrous sulphate are deposited in the protoplasm of the cells containing chlorophyll.

My friend Mr. R. S. Wray (Honoursman in Botany) of the University of London draws my attention to another supposition, namely, that these crystals may not exist as crystals in the *living* plants, but that the ferrous sulphate may exist in a dissolved condition in the protoplasm of the cells, the crystals found in the microscopical sections being produced by post-mortem changes. I shall test the truth of this idea by further microscopical investigations on such plants as Protococcus, Spirogyra, &c., growing in proper solutions containing

ferrous sulphate, and I shall then be able to see whether these crystals are deposited in the living protoplasm of the chlorophyll cells.

In the sections examined under the microscope, the crystals were always to be found near to the chlorophyll corpuscles, and there may be some probability in the supposition that these crystals act as reserves for the formation of the green colouring matter chlorophyll. I shall presently examine other plants grown with an iron manure. As I stated in my first paper on this subject, it is highly probable that a soluble salt of iron added to a soil in which certain plants grow is beneficial to their healthy condition.

I do not for a moment suppose that the ferrous sulphate originally applied to the soil would last as soluble $FeSO_4$ for the lapse of ten or eleven months; atmospheric influences would probably oxidise it to the ferric condition; but one thing is certain, that the iron must be absorbed by the roots in a dissolved condition, and subsequently find its way into the protoplasm of the cells containing chlorophyll, either being deposited as crystals, or remaining dissolved in the substance of the protoplasm.

XXIX.—*On Condensations of Compounds which contain the Dicarbonyl-group with Aldehydes and Ammonia.*

By Francis R. Japp, M.A., Ph.D., Assistant Professor of Chemistry in the Normal School of Science, South Kensington.

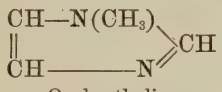
In a former communication (this Journal, 1883, Trans., 9; more fully *Ber.*, **15**, 2410) I developed at some length my interpretation of the above series of condensations, the experimental details of the study of which are contained in various papers published in this Journal during the last two years by myself in conjunction with others. I pointed out the bearing of this interpretation upon the question of the constitution of lophine, glyoxaline, and allied compounds. I further showed that the interpretation which Radziszewski (*Ber.*, **15**, 1493) sought to substitute for mine, though plausible enough when Radziszewski's reactions alone are considered, is hardly tenable when these are taken in conjunction with other reactions of the same class described by me.

Radziszewski has since described (*Ber.*, **15**, 2706) a new synthesis of Wallach and Schulze's paraoxalmethyline by the condensation of glyoxal with acetaldehyde and ammonia:—

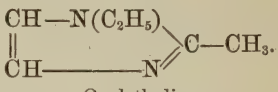
$$\underset{\text{Glyoxal.}}{C_2H_2O_2} + \underset{\text{Acetaldehyde.}}{C_2H_4O} + 2NH_3 = \underset{\text{Paraoxalmethyline.}}{C_4H_6N_2} + 3OH_2.$$

The author had not, at the time of sending in his communication, seen my paper on the interpretation of the above class of condensations,* a class to which this reaction belongs. In that paper (*Ber.*, **15**, 2420) I made some suggestions concerning the constitution of the oxalines. As I consider that the experimental result obtained by Radziszewski furnishes a confirmation of the views there expressed, I desire to develop these somewhat more fully, and to point out that by adopting the formulæ for glyoxaline and oxalmethyline (methylglyoxaline) proposed by me, the constitution of the whole of the important compounds discovered by Wallach admits of explanation.

Starting therefore with the formula of oxalmethyline given by me in the above paper, and formulating oxalethyline on the same type,† we arrive at the two formulæ:—

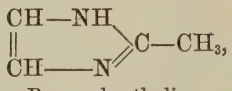


Oxalmethyline
(identical with methylglyoxaline).



Oxalethyline.

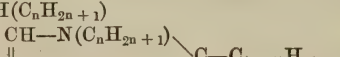
The most probable formula for paraoxalmethyline, a compound which, as Wallach and Schulze have shown, is formed from the first of these by intramolecular change, from the second by elimination of ethylene, would be—



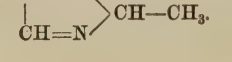
Paraoxalmethyline.

and this, if my views concerning the above class of condensations are correct, is the formula of a compound which would be formed by the action of acetaldehyde and ammonia upon glyoxal.‡

* I take for granted that my reservation of the further study of these condensations (this Journal, 1882, 329) has escaped Radziszewski's notice.

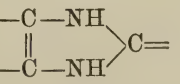
† The general formula of an oxaline obtained from a di-substituted oxamide of the formula $\begin{matrix}CONH(C_nH_{2n+1})\\ |\\ CONH(C_nH_{2n+1})\end{matrix}$, in which *at least one* of the alcohol-radicles must be primary, would be  .

‡ Radziszewski (*loc. cit.*) attributes to paraoxalmethyline the constitution —

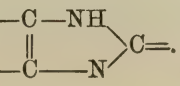


The whole question between my *anhydro-base formulæ* (cf. this Journal, 1883, Trans., 9) and Radziszewski's *symmetrical formulæ* for compounds of this class (the oxalines, lophine, &c.) resolves itself into the simple question whether glyoxaline, the lowest member of the series, contains a replaceable hydrogen-atom directly attached to nitrogen. A proof that this is the case would decide in favour of the anhydro-base formula. Now from the experimental evidence adduced by Wallach and by Radziszewski, there can be little doubt that the oxalines are nothing more than glyoxaline in which one or more hydrogen-atoms have been replaced by alcohol-radicles, and I think there are experimental facts which show that in some of these compounds the radicle is directly attached to nitrogen. One such fact, which is absolutely conclusive as regards the compound in question, is that Wallach and Schulze obtained ethyloxamide by the oxidation of chloroxalethyline. The boiling point of methylglyoxaline (a compound obtained by the action of methyl iodide upon glyoxaline) also renders it probable that this compound is derived from glyoxaline by the replacement of imidic hydrogen by methyl; for whilst para-oxalmethyline, as a homologue of glyoxaline in which the methyl-group is attached to carbon, boils 13° higher than glyoxaline, methyl-glyoxaline boils 58° lower. This lowering of the boiling point in the conversion of a secondary into a tertiary amine- or amide-group has been observed before in the case of diamines and diamides (cf. E. Fischer, *Annalen*, **190**, 155; Michler, *Ber.*, **8**, 1665). Radziszewski's argument that glyoxaline and lophine do not contain an NH-group because they do not react with acid chlorides and anhydrides, has been refuted by anticipation in my previous paper (*Ber.*, **15**, 2420). Lophine and glyoxaline behave in this respect exactly like the class of compounds to which they belong—the anhydro-bases of Hübner. Anhydrobenzdiamidobenzene may, as Hübner has shown, be heated with benzoyl chloride to 260° without alteration.

In the above connection I would call attention to the evidence afforded by the work of Ladenburg and Rügheimer on condensations of orthotolylenediamine (*Ber.*, **12**, 952) of the ease with which the symmetrical complex—



passes, under the influence of heat, into the unsymmetrical anhydro-complex—



This is the change which I have represented as occurring when amarine is transformed by heating into lophine (*Ber.*, **15**, 1270).*

XXX.—*On some Condensation-products of Aldehydes with Acetoacetic Ether and with Substituted Acetoacetic Ethers.*

By F. E. Matthews.

Some time since Claisen (*Ber.*, **12**, 345) showed that acetoacetic ether enters into reaction with aldehydes to form condensation-products. The reaction takes place in the manner shown by the general equation—

$$R.COH + C_6H_{10}O_3 = C_6H_8(CH.R)O_3 + H_2O$$

with the greatest readiness, since it occurs at a temperature of 0° C., and by the simple absorption of hydrochloric acid gas. Although the products obtained in this manner have until now not been further studied, there is scarcely any doubt as to the manner in which the reaction takes place.

The combination between acetic aldehyde and acetoacetic ether could certainly take place in various ways:—The aldehydic oxygen could combine with the hydrogen of the acetoacetic ether, or the ketonic oxygen of the latter with the hydrogen of the methyl-group of the aldehyde. The full and complete analogy which, however, takes place in the reaction when benzoic aldehyde is substituted for acetic aldehyde shows clearly—since benzoic aldehyde does not contain any hydrogen-atoms capable of easy reaction, as is the case with ordinary aldehyde—that the aldehyde-residue, R.CH, is really introduced into the molecule of acetoacetic ether.

The next question was whether the CH_3, or the CH_2-group of the acetoacetic ether parts with its hydrogen to the oxygen of the aldehyde. Claisen's researches also made this sufficiently clear. He found that malonic ether, which possesses a methylene-group similar to that of acetoacetic ether, reacts in a precisely similar manner, and with the same ease as acetoacetic ether. The analogy of the two reactions points clearly to the fact that the methylene-group of the acetoacetic ether takes part in the reaction, and not the methyl-group.

* I take this opportunity of rectifying an omission. It had till lately escaped my notice that the amarine formula given in the paper here referred to, had already been proposed as an *alternative* formula by E. Fischer. The formula is not given in Fischer's published work on amarine, but is introduced incidentally in a paper on furfural (*Annalen*, **211**, 217).

It seemed to me that it would be interesting to study this reaction in at least two directions; firstly, to see whether the reaction is a general one, taking place between all the various classes of aldehydes and acetoacetic ether, and secondly, what is the behaviour of various substituted acetoacetic ethers, such as mono- and diethyl-, and dichlor-substituted ethers with aldehydes.

To clear up these two points I have studied the following reactions:—

Condensations of acetoacetic ether with—

Isobutylic aldehyde.
Valeric aldehyde.
Chloral.
Furfural.
Acroleïn.

Relations of di-substituted acetoacetic ethers to benzoic aldehyde:

Benzoic aldehyde and acetodiethylacetic ether.
„ „ „ acetodichloracetic ether.
„ „ „ acetobenzylideneacetic ether.

Relations of monosubstituted acetoacetic ethers to benzoic aldehyde:

Benzoic aldehyde and acetomonoethylacetic ether.

Condensation of Isobutylic Aldehyde with Acetoacetic Ether.

Acetoacetic ether and isobutylic aldehyde were mixed in molecular proportions, and into the mixture, thoroughly cooled with a mixture of ice and salt, hydrochloric acid gas was conducted. The gas was for a considerable time entirely absorbed, whilst the mixture became darker in colour, and deposited an underlayer of aqueous hydrochloric acid, which on continuing the stream of gas, disappeared after some time. The mixture was allowed to stand for 18 hours in ice-water, after which it was poured into water, when the ether separated out as a yellow layer on the surface. It was washed with water and caustic soda, dried over chloride of calcium, and afterwards distilled. During the first portion of the distillation, an immense amount of hydrochloric acid gas was evolved. The evolution of gas ceased at about 210°, between which and 230° nearly the whole of the product distilled over. The portion 210—230° was several times redistilled, and at last boiled almost entirely between 219—222°. This portion gave on analysis the following result:—

0·1133 gram substance gave 0·2712 gram CO_2 and 0·0870 gram H_2O.

	Calculated for $C_{10}H_{16}O_3$.	Found.
C	65·22	65·28
H	8·69	8·53

This substance, *acetoisobutylidene-acetic ether*, is, when freshly prepared, an almost colourless liquid. It boils at 219—222° (thermometer in vapour to 140°), has a very pleasant smell somewhat similar to that of peppermint, and is slightly decomposed at each distillation, leaving a residue of higher boiling substances. In chloroform solution it combines directly with bromine; on warming it with alkalis the smell of isobutylic aldehyde becomes at once apparent, and the compound seems to be resolved into that aldehyde and acetoacetic ether.

Condensation of Valeric Aldehyde with Acetoacetic Ether.

This reaction was conducted in a precisely similar manner to the former one. The same evolution of hydrochloric acid gas was noticed, and it seems that all these unsaturated substances combine in the cold with hydrochloric acid to form addition-products, which become decomposed during the distillation:—

The substance gave the following results on analysis:—

I. 0·1796 gram substance gave 0·4392 gram CO_2 and 0·1496 gram H_2O.

II. 0·1706 gram substance gave 0·4154 gram CO_2 and 0·1402 gram H_2O.

	Calculated for $C_{11}H_{18}O_3$.	Found.	
		I.	II.
C	66·67	66·69	66·41
H	9·09	9·25	9·13

The yield of pure substance is exceedingly good. From 50 grams of valeral I obtained 40 grams of the pure ether.

Acetoisoamylidene acetic ether is an almost colourless liquid. It is slightly decomposed on distillation. It has an odour somewhat resembling that of strawberries. It boils at 237—241°. Sp. gr. (at 15° compared with water at the same temperature) 0·9612. It reacts with bromine and alkalis in a precisely similar manner to the preceding substance.

Condensation of Chloral with Acetoacetic Ether.

Dry hydrochloric acid appears scarcely to act upon a mixture of chloral and acetoacetic ether. A mixture of these substances saturated

with hydrochloric acid became gradually thick, and its colour changed to a yellow-green. After standing for several days, however, it was subjected to washing and distillation, and only a very small fraction, about 2 or 3 per cent., boiled at a temperature above 200°. I therefore tried another method of condensation, viz., that by means of acetic anhydride, and by this method the condensation appears to take place quantitatively.*

Chloral, acetoacetic ether, and acetic anhydride in molecular proportions were heated in sealed glass tubes for 6—8 hours, at a temperature of 140—160°. The contents of the tube were coloured light brown, and on opening the tubes there was a slight pressure due to liberated carbonic acid. The product was directly subjected to distillation, and at first a considerable amount of acetic acid distilled over. After this the thermometer rose rapidly to 230°, between which and 250° a considerable amount of liquid distilled over. There were, however, all the signs that destructive distillation had taken place, and at the next operation the distillation was performed under reduced pressure. Almost the whole of the product distilled from 160—170°, at a pressure of 35 mm., and by fractioning several times more, the substance was obtained pure, and boiling constantly at 154—158°, at a pressure of 24—26 mm.

Analysis.

I. 0·2363 gram substance gave 0·3276 gram CO_2 and 0·0856 gram H_2O.

II. 0·2629 gram substance gave 0·3633 gram CO_2 and 0·1002 gram H_2O.

III. 0·3320 gram substance gave 0·5500 gram AgCl.

	Calculated for $C_8H_9Cl_3O_3$.	Found. I.	II.	III.
C	36·99	37·81	37·68	—
H	3·47	4·02	4·23	—
Cl	41·04	—	—	40·98

The substance *acetotrichlorethylidene acetic ether* (α-acetotrichlor-

* In order to convince myself that this method of condensation was of general application, I have made by its means both benzylidene-malonic and benzylidene-acetoacetic ether, and in both cases I obtained an almost theoretical amount of product. Crismer, in a paper read before the Belgian Academy, entitled "La Réaction de Perkin," found that neither hydrochloric nor sulphuric acid acts in the way he wished—in condensing a mixture of aldehyde and malonic ether. Hydrochloric acid has no reaction at all, and with sulphuric acid the action is of too violent a description. By using the above method, however, he obtained most easily ethylidene-malonic ether, isomeric with the ethers of ita-, citra-, and mesa-conic acids.

crotonic ether) is a thick colourless oil, with an odour which reminds one strongly of chloral. Its specific gravity (15°) is 1·3420. Bromine acts upon the chloroform solution only with difficulty, and on the chloroform solution being evaporated, a thick oil was left behind, which after a long time solidified to a mass of prismatic crystals.

Condensation of Furfural with Acetoacetic Ether.

In this condensation, as was to be expected beforehand, hydrochloric acid could not be used as a condensing agent, on account of its powerful action upon furfural. The method of condensing by means of acetic anhydride gave on the contrary excellent results. The reaction was carried out in a similar manner to the previous one. After the acetic acid had distilled over, the distillation was continued under reduced pressure, and the product after being twice fractioned, boiled at 188—189°, at a pressure of 29—32 mm., and solidified at once to a crystalline mass.

Analysis.

I. 0·2302 gram substance gave 0·5344 gram CO_2, and 0·1190 gram H_2O.

II. 0·2036 gram substance gave 0·4738 gram CO_2, and 0·1050 gram H_2O.

III. 0·1633 gram substance gave 0·3843 gram CO_2, and 0·0870 gram H_2O.

	Calculated for $C_{11}H_{12}O_4$.	Found. I.	II.	III.
C	63·46	63·31	63·46	63·79
H.....	5·77	5·75	5·73	5·88

Analyses I and II were made on the substance purified by distillation. III was made on a portion crystallised from light petroleum.

This substance, *acetofurfurylidene acetic ether* (α-acetofurfuracrylic ether) is colourless and crystalline, easily soluble in chloroform, acetic acid, alcohol, and benzene. Light petroleum and ether dissolve it only when boiling, and it crystallises from these solvents in splendid large crystals, which possess the property of double refraction in the highest degree.

The boiling point of the ether has already been given, and it melts at 62—62·5°.

A dibromide was made, but as it showed no tendency to crystallise it was not further investigated.

Acroleïn and Acetoacetic Ether.

I endeavoured to effect the condensation of acroleïn with acetoacetic ether by means of the hydrochloric acid method. The substances

seemed to combine, but the product was always decomposed on distillation, even in a vacuum. At this time I did not know of the acetic anhydride method of condensation, so that until now I have obtained only negative results in the formation of aceto-allylideneacetic ether.

Behaviour of Di-substituted Acetoacetic Ethers with Benzoic Aldehyde.

Condensation of Diethylacetoacetic Ether and Benzoic Aldehyde.

Pure diethylacetoacetic ether and benzoic aldehyde were mixed together in molecular proportion, and saturated with hydrochloric acid. After some time the mixture began to get darker in colour, and at length became intensely dark red. It was left at rest for four days, and was then poured into ice-water, washed with soda-solution, dried over calcium chloride, and distilled under reduced pressure. During the distillation an immense amount of hydrochloric acid was given off, as in the condensations before mentioned, but it at once became evident that the greater part of the mixture had not entered into any reaction at all. At a pressure of 3 mm., more than two-thirds of the oil distilled over below 100°, and it was recognised as only a mixture of the unaltered ether and benzoic aldehyde. A small portion of the substance, however, came over at 200—205° (pressure 3 mm.). This was analysed and found to contain about 1 per cent. too little carbon for the substance $C_{17}H_{22}O_3$, and also to contain a small amount of chlorine. Fortunately it solidified after some time, and after crystallisation from petroleum was again analysed.

I. 0·2204 gram gave 0·5999 gram CO_2 and 0·1607 gram H_2O.
II. 0·1798 „ „ 0·4912 „ „ 0·1308 „ „

	Calculated for $C_{17}H_{22}O_3$.	Found. I.	Found. II.
C	74·45	74·23	74·50
H	8·03	8·10	8·08

The substance $C_{17}H_{22}O_3$ (cinnamyldiethylacetic ether) is a colourless crystalline body melting at 101—102°. It is easily soluble in ether and chloroform, slightly soluble in cold alcohol and ligroïn, and is best prepared pure by crystallisation from a boiling solution of the last solvent. The mechanism of the reaction is that the CH_3-group in diethylacetoacetic ether, being adjacent to a CO-group, is, as Claisen and Claparède (*Ber.*, **13**, 349; **14**, 2460) have shown in the cases of aldehyde, acetophenone, mesityl oxide, and pyruvic acid, capable of condensation with benzoic aldehyde. It seems that the position of the CO-group or groups is the principal influence in determining the

mode of condensation between ketonic compounds and aldehydes. The methylene-groups in malonic and acetoacetic ethers are directly combined with two CO-groups, and hence the combination takes place with the greatest ease. With pyruvic acid and diethylacetether, the condensation takes place with much greater difficulty, as the only points capable of condensing are directly united to but one CO-group. In the case of acetoacetic ether I found the condensation to be complete in 18 hours, whilst with the diethyl ether only about 25 per cent. had condensed after a lapse of four days.

A solution of cinnamyl diethylacetic ether in chloroform at once decolorises bromine, and on spontaneous evaporation of the chloroform, leaves behind an oil which finally solidifies. It was recrystallised from ligroïn, and gave on analysis the following figures :—

0·1343 gram substance gave 0·2318 gram CO_2, and 0·0604 gram H_2O.

0·1306 gram substance gave 0·1120 gram AgBr.

	Calculated for $C_{17}H_{22}Br_2O_3$.	Found. I.	Found. II.
C	47·00	47·07	—
H	5·07	5·16	—
Br.....	36·87	—	36·49

This dibromide crystallises in small colourless prisms, which melt at 54—55°, and are distinguished from the original ether by their easy solubility in alcohol and petroleum.

I have also attempted to effect the following condensations of di-substituted acetoacetic ethers, dichloroacetoacetic ether with benzoic and acetic aldehydes, and benzylideneacetoacetic ether with the same aldehydes. I have tried all the methods of condensation with which I was acquainted in these cases, but in no case was I able to isolate any condensation-product, and in fact with the dichlorinated ether I was unable to find any trace whatsoever of a reaction. The dichlorether is therefore an exception to the rule that all substances which have a CH_3-group directly combined with a CO-group are capable of forming compounds with benzoic aldehyde, with elimination of one molecule of water.

Behaviour of Mono-substituted Acetoacetic Ethers with Benzoic Aldehyde.

Condensation of Monoethylacetoacetic Ether and Benzoic Aldehyde.

This condensation was effected similarly to that with the diethyl ether. The product, however, did not boil so constantly as in the

former case, and as it showed no tendency to solidify, it was not so easy to purify. After the first distillation it contained 2—3 per cent. of chlorine, and on every subsequent distillation it was slightly decomposed, and on analysis always showed an excess of carbon. It was, however, obtained in an approximately pure condition, and gave on analysis the following numbers:—

I. 0·246 gram substance gave 0·6694 gram CO_2, and 0·1678 gram H_2O.

II. 0·1878 gram substance gave 0·5092 gram CO_2, and 0·1249 gram H_2O.

	Calculated for $C_{15}H_{18}O_3$.	Found. I.	Found. II.
C	73·17	74·21	73·94
H	7·32	7·58	7·39

The substance in the purest state I obtained it, is a yellow pleasant-smelling oil, boiling at about 210° under a pressure of 22 mm.

It is evident that if this condensation is analogous to that of the diethyl ether, the compound must still contain one hydrogen-atom possessing the property of being replaced by sodium in the same way as aceto-acetic ether; and further, that if this atom of hydrogen be replaced by a C_2H_5-group, the identical cinnamyldiethylacetic ether will be obtained. I therefore acted upon the cinnamylmonoethylacetic ether, first with sodic ethylate, and afterwards with ethyl iodide, and obtained a substance which on recrystallisation from ether, melted at 101—102°, and gave on analysis the following numbers:—C 74·53 per cent., H 8·31 per cent., whereas theory requires C 74·45 per cent., and H 8·03 per cent. The substance was identical in all its properties with, and in fact was cinnamyldiethylacetic ether. I may here remark that Crismer (*loc. cit.*) has found that monoethylmalonic ether is quite incapable of condensing with benzoic aldehyde.

In conclusion I wish to point out—1st. That acetoacetic ether is capable of condensing with aldehydes of all descriptions, and that the condensation takes place only in the methylene-group, but with the greatest ease. 2nd. That mono- and di-substituted acetoacetic ethers (with the exception of the dichlorether) are capable of condensing with benzoic aldehyde, but that the condensation is very much more difficult to effect, and takes place only in the methyl-group.

XXXI.—*Contribution to the Chemistry of "Fairy Rings."*

By Sir J. B. Lawes, Bart., LL.D., F.R.S., J. H. Gilbert, Ph.D., F.R.S., and R. Warington.

The circles of dark-green grass which frequently occur on pasture land, and have long been known by the name of "Fairy Rings," have naturally attracted the attention of botanists and vegetable physiologists, and various explanations of their occurrence have been given. It has long been supposed that the luxuriant growth of grass constituting the ring is connected with the growth and decay of fungi, which so serve as manure for the grasses which succeed them. Among the numerous explanations of the fact that the growth assumes the form of an extending ring, perhaps the one which for some time received the greatest attention, was that based on the theory of Decandolle, according to which the excretions of a plant are prejudicial to the growth of plants of the same description. It was supposed that the excretions of fungi were detrimental to their recurrence on the same spot, and hence they developed only externally to the ring of their previous growth.

The first explanation of the luxuriant growth of the rings, put forward from a more purely chemical point of view, was that of Professor Way, in a paper "On the Fairy Rings of Pasture, as illustrating the use of Inorganic Manures," which was read in the Chemical Section of the British Association at Southampton in 1846, and was published in the *Journal of the Royal Agricultural Society of England*, **7**, 549. He analysed the ash of some of the fungi, and also of the grass of a fairy ring. From the results of these analyses he explains the growth of the fairy rings as follows:—"A fungus is developed on a single spot of ground, sheds its seed, and dies. On the spot where it grew it leaves a valuable manuring of phosphoric acid and alkalis, some magnesia, and a little sulphate of lime. Another fungus might undoubtedly grow on the same spot again; but upon the death of the first the ground becomes occupied by a vigorous crop of grass, rising like a phœnix, on the *ashes* of its predecessor." The growth of the grass as an extending ring, and not as a disc, he further explains by the fact of the removal of the grass, and with it "the greater part of the inorganic materials which the fungus had collected." He adds, that the nitrogen of the fungus must not be left out of consideration, but that he believes—"it is to the inorganic elements that the effect is chiefly to be ascribed."

Buckman, on the other hand, whilst admitting that fungi are fre-

quently found on or just outside the ring, considers their occurrence by no means essential to the formation of the ring, and that it may be produced by any cause unfavourable to the growth of a circular disc of grass. At the same time he says—"there is reason to think that rings to which the fungi have not become attached soon break up" (*Veterinarian*, May and June, 1870).

Almost from the commencement of the Rothamsted experiments, the circumstances of the development of fairy rings have been observed with much interest, as affording a striking example of what may be called "natural rotation." It was thought that if the source of the nitrogen of the fungi growing in fairy rings were determined, some light might perhaps be thrown on the source of the nitrogen of the Leguminosæ, which are grown separately, in rotation with the cereals and other crops, or in association with the grasses in the mixed herbage of grass land. In a Rothamsted paper in 1851 (*Jour. Roy. Ag. Soc.*, **12**, 32), the subject was referred to as follows:—"A beautiful illustration of the dependence for luxuriant growth of one plant upon another of different habits, such as we have shown above, may be found in the case of the 'fairy rings,' where the fungus, by virtue of its extraordinary power of rapidly accumulating nitrogen from the atmosphere during its growth, taking up the minerals which the grasses, from their more limited power in this respect could not appropriate, provides an abundance of the nitrogenous manure so effective in the growth of the grasses which are observed to spring up with great luxuriance wherever the fungus has grown or fallen."

Here, then, it was assumed that it was the nitrogen, rather than the ash-constituents of the fungus, to which the manuring action was mainly to be attributed. Even at that time the characteristic effects of mineral and nitrogenous manures respectively, on the growth of gramineous crops, were sufficiently established by field experiments to leave no doubt that the dark colour and the luxuriant growth of the grasses on the rings were intimately connected with a liberal supply of nitrogen as manure. But it will be observed that the source of the nitrogen of the fungi was then supposed to be the atmosphere.

Since that time much directly experimental and other evidence has been acquired as to the sources of the nitrogen of green-leaved plants; and, although absolute proof is still wanting on some points—and it might well be that plants of such opposite characters as fungi might have a different source—yet doubt as to the atmospheric source of their nitrogen gradually increased. Accordingly, in 1874, an attempt was made to obtain direct experimental data on the subject. Samples of soil were taken of a fixed area and to a fixed depth within, on, and outside a fairy ring; and in each the nitrogen was determined.

The results showed the lowest percentage of nitrogen in the surface soil within the ring, a higher percentage under the ring, and a higher still outside it. The obvious conclusion was, that the soil within the ring had lost nitrogen by the growth of the fungi, and the subsequent luxuriant growth and removal of the grasses. But so important a conclusion required confirmation. Accordingly, in a short paper by one of us entitled "Note on the Occurrence of Fairy Rings," published in 1875 (*Jour. Linn. Soc. Bot.*, **15**, 17), the general indication only was stated, reserving the publication of the numerical results until they should be confirmed. The soils of other fairy rings have since been collected and investigated, and it was intended to extend the inquiry further; but, owing to the unfavourable weather of the last few years, the rings which had been under examination have disappeared. Under these circumstances, and as the general bearing of the results already obtained is unmistakable, it has been decided to put on record both the earlier and the later results, without waiting for further repetition or extension.

Before entering upon a consideration of the experimental results in question, it will be well to refer a little more in detail to some of the circumstances of the occurrence of a fairy ring.

It is probable that the fungi growing on grass land owe their occurrence, in the first instance, to the accidental droppings of animals (or birds); and it seems to depend on the conditions of soil, season, and association, whether the growth is limited to the original spot, or whether it extends, and an annually increasing ring is formed. If the soil be rich, or highly manured, or the season very favourable for luxuriance of the general herbage, the probability is that the fungi will not be reproduced, and a patch only will be developed. It is under opposite conditions, that is, where the soil is poor, that the development of rings is generally observed.

The growth of fungi being once established from some extraneous cause, such as above referred to, they will on decay supply a rich nitrogenous and mineral manuring to the adjacent herbage. A patch of dark-green luxuriant grass succeeds. This being cut or eaten off, the soil becomes the more exhausted the more luxuriant has been the growth. Accordingly the vegetation within the ring is generally less luxuriant than that outside it. In the case of mere patches, some examinations of the soil in spring and autumn have not shown a marked development of mycelium. But on digging into the turf immediately outside a ring, it is generally found penetrated by a white cobweb-like mycelium, extending to a depth of several inches, and sometimes even to a foot or more. When the mycelium is abundant, the soil is remarkably dry, and can with difficulty be wetted, as if it were greasy. The mycelium is most abundant in the soil

just outside the ring, or at the outer edge of it. If the season be favourable, an aboveground growth of fungi will appear in the spring or autumn. These fructify, and, by scattering their spores, give rise to a further growth of mycelium. The fungus thus spreads into fresh ground, and the rings extend outwards, so long as the circumstances of the soil and season are favourable. Sometimes, however, fungi are found growing in the midst of the band of luxuriant grass. In such cases it would appear that the increased growth of the grass is due to the decay of the mycelium, or to its action on some of the organic compounds in the soil.

In the paper above referred to, the relative development of fairy rings, and of fungi generally, on the differently manured plots of meadow land in the park at Rothamsted is described. Among the more than twenty differently manured plots, fairy rings have occurred on only two, neither of which has received either nitrogen or potash as manure for many years. The one is annually manured with superphosphate of lime alone, and the other with a mixture of superphosphate and the sulphates of sodium and magnesium. Quite consistently with what is commonly recognised as to the conditions most favourable for the development of fairy rings, the general vegetation on these plots is of a very restricted character. Where nitrogenous manures are applied, and the luxuriant growth of the grasses is thereby promoted, no fairy rings have occurred, and the appearance of fungi is rare. As fairy rings thus developed only where the growth of the grasses and their associates was extremely limited (owing to deficient supply of nitrogen or of potash, or of both, in a condition available to them), the questions were suggested—How far the fungi prevail simply in virtue of the absence of adverse and vigorous competition?—whether they live to a greater or less extent as parasites, and so at the expense of the sluggish underground growth of the plants in association with them?—whether they have the power of acquiring nitrogen in some form from the atmosphere?—or, lastly, whether they assimilate nitrogen from the soil itself, existing there in a condition not available to the plants growing in association with them?

Of the composition of the mycelium but little is known, and it is to be supposed that it would vary considerably at different periods of its development. On several occasions it has been found at Rothamsted to leave a very considerable incombustible residue, consisting chiefly of calcium carbonate, which is presumably the result of the destruction of calcium oxalate.

The general composition of the aboveground growth has been determined by Fleury in the case of two of the fairy ring fungi (*Rép. Pharm.*, 31, ann. 73, p. 261). The following is an abstract of his results:—

TABLE I.—*Percentage Composition of two Fairy Ring Fungi.*

Species.	Water.	Nitrogen reckoned as albuminoïds.	Fatty matter.	Soluble carbohydrates.	Fibre.	Ash.
			In Fresh Substance.			
Marasmius oreadum	91·75	2·93	0·19	3·59	0·67	0·87
Agaricus prunulus..	89·25	4·11	0·14	4·08	0·81	1·61
			In Dry Matter.			
Marasmius oreadum	—	35·57	2·40	43·34	8·12	10·57
Agaricus prunulus..	—	38·32	1·38	37·77	7·53	15·00

The following is the composition of the ash of one species of fairy-ring fungus as determined by Professor Way (*Jour. Roy. Ag. Soc.*, **7**, 550, 1846):—

TABLE II.—*Percentage Composition of the Ash of* Agaricus prunulus.

Ash in 100 dry.	Per cent. in Ash.								
	K_2O.	Na_2O.	CaO.	MgO.	P_2O_5.	SO_3.	SiO_2.	Cl.	CO_2.
6·38	55·10	3·54	1·35	2·20	29·49	1·93	1·09	0·25	3·80

The composition of the fairy ring fungi appears from these analyses to be very similar to that of other fungi which have been analysed; and it may be mentioned that one of the species examined by Fleury, the *Marasmius oreadum*, occurs on the rings at Rothamsted. The fungi contain a large proportion of nitrogenous matter, amounting to more than one-third of their dry substance; and their ash is extremely rich in both potash and phosphoric acid, but especially in potash. Yet it will be remembered that fairy rings developed only on two of the experimental plots at Rothamsted, neither of which had received either nitrogen or potash as manure for many years, and where the growth of the grasses was extremely meagre.

It is evident from the very restricted vegetation of these plots, from the richness in nitrogen of the fungi, and from the great luxuriance of the grasses which succeed them, that the fungi were

able to obtain an amount of nitrogen from some source greatly in excess of that which was available to the associated herbage. What is the source of this nitrogen? Has the fungus the power of assimilating it largely from the atmosphere? or has it the power of taking it up from the soil in a manner, or in a degree, which the grasses and other green-leaved plants do not possess? The object of the experiments now to be described was to obtain an answer to these questions.

We will first give a brief history of the various samples of soil which have been collected and analysed, and afterwards direct attention to the results which have been obtained.

The Grove Paddock Fairy Ring.

The samples of soil were taken on May 19th, 1874. The ring, which then consisted of a half circle several yards in diameter, and had been observed to increase during the past few years, was near a hedge and some trees, and the soil was much permeated by roots. The band of grass forming the ring was about 2 feet wide, and of a dark bluish-green colour. The grass was of a much lighter colour both within and outside the ring, and rather lighter within than outside. Samples of the soil were taken at three points: 1. Two feet within the ring. 2. In the centre of the ring-band. 3. Two feet outside the ring. In each case a sample of the first, and of the second 9 inches of depth, was taken.

The mode of collecting the soil samples was that which has been employed for many years at Rothamsted. A frame of strong sheet iron 6 inches square, 9 inches deep, open at the top and bottom, and having a strong rim outside the upper edge, was driven into the ground until the upper edge was level with the surface. The contents were then carefully taken out, and constituted the sample of the first 9 inches of depth. The soil round the frame was then removed to the depth of its lower edge, it was again driven down into the soil, and the contents taken out, these representing the second 9 inches of depth.

The sample of the first 9 inches of soil taken on the ring was remarkably dry, and much paler in colour than that of the sample from the same depth either from without or within the ring, that from outside the ring being much the darkest of the three. Mycelium was found to extend to the depth of a foot or more. This is a somewhat greater depth than usual, probably accounted for by the large amount of organic *débris* from the roots of the hedge, and two large ash trees, one on either side.

The Broadbalk Field Fairy Ring.

This was a small imperfect ring forming about two-thirds of a

circle. The ground within the circle had been disturbed in recent years, and there was doubt how far the disturbance had extended.

The first series of samples was taken on June 18th, 1877. The ring was then covered with a luxuriant growth of grass, interspersed with which were a few fungi. The samples of soil taken were: 1. Within the ring, about 14 inches from it. 2. On the ring. 3. Just outside the ring. 4. Quite outside it, about 16 inches from it. A rather considerable amount of mycelium was found in the soil taken from the ring, extending from the surface to a depth of 5 or 6 inches. In the sample taken just outside the circle a little mycelium was found.

A second series of samples was taken on September 15th of the same year. The ring had widened since June, and was again covered with a luxuriant growth of grass. The samples taken were: 1. Within the ring, 18 inches from it. 2. On the ring. 3. Outside the ring, about 15 inches from it. The soil from the ring contained a comparatively small amount of mycelium, extending about 4 inches from the surface.

The samples of soil from this ring, and from those subsequently experimented upon, were not taken with the iron frame already described, but with a steel cylinder, $2\frac{1}{2}$ inches in diameter, and 12 inches long, fixed at the end of a stout iron rod. The cylinder was driven into the ground until its upper edge was level with the surface; when withdrawn it contained a solid core of soil, which was removed through a slit in the side which was covered during the working. The advantage of this mode of soil sampling is its simplicity; but the objections to it are that the quantities of soil brought up are more irregular, and do not therefore so nearly represent the depth intended as when the wider square frame is used. Owing to the narrowness of the cylinder the soil rises within it with considerable difficulty, becoming much consolidated below, and when the cylinder is drawn up it is found to be but partially filled. In any case, however, it would be inappropriate to calculate quantities of soil, or of any of its constituents, over a given area to a given depth, from single samples; and as the object in the present instance was simply to compare the percentage composition of different samples of soil collected at the same time and in the same manner, the imperfections of the method above referred to are of less consequence.

The Park Fairy Rings.

It has been already mentioned that fairy rings were numerous on the plot of experimental meadow land in the park which was continuously manured with superphosphate of lime alone. A perfect ring on this plot was selected for examination. The samples of soil

were taken on September 19th, 1877. The band of grass forming the ring was about 3 feet wide, and very luxuriant, but no aboveground growth of fungi was then observed. The samples taken were: 1. Within the ring, about 4 feet from the centre of the band. 2. On the ring, in the middle of the band. 3. On the ring, at its outer edge. 4. Quite outside the ring. In the soil from the centre of the band but little mycelium was found; in that from the outer edge, mycelium was abundant at the surface, but extended very little below it.

In the following spring (1878) this ring having extended considerably in width, and its outline having become indistinct, no further samples were taken from it; but another partial ring on the same plot was selected for experiment. The soil of this second ring was sampled on April 25th, 1878. The band was then about 2 feet wide. The samples taken were: 1. Within the ring, about $2\frac{1}{2}$ feet from it. 2. On the ring towards the inside. 3. On the ring towards the outside. 4. Outside the ring, about $1\frac{1}{2}$ foot from it. In the soil taken from the ring towards the outside of it, mycelium was fairly developed, and extended 5 or 6 inches below the surface. Here the soil was drier, and of a lighter colour, than at the other points.

Preparation and Analysis of the Soil Samples.

From all the samples, the stones, roots, and other observable organic residue were carefully picked out, and the remaining soil was reduced to fine powder. The samples from the Broadbalk Field and the Park Fairy Rings were partially dried by exposure in a thin layer in a warm room immediately after being received in the laboratory; but those from the Grove Paddock were not so prepared. As a necessary means of calculation, especially of the percentage of water, the weights of the fresh samples, and of their separated parts, were taken in all cases excepting those of the soils from the Broadbalk Field.

The following table shows the percentage of water, lost on drying at 100° C., and calculated on the total fresh soil (excluding stones), in the cases of all the samples from the Grove Paddock, and the Park Fairy Rings.

TABLE III.—*Percentage of Water in Fresh Soil as collected, exclusive of Stones.*

	Surface soil.	Subsoil.
Grove Paddock Fairy Ring Soils, May 19, 1874.		
Within the ring	16·03	15·68
On the ring	12·58	12·30
Outside the ring	15·71	16·24
The Park Fairy Ring Soils, September 19, 1877.		
Within the ring	22·80	17·04
On ring (centre)	19·29	13·13
On ring (outer edge)	18·50	13·23
Just outside ring	23·33	15·03
The Park Fairy Ring Soils, April 25, 1878.		
Within the ring	26·34	19·21
On ring (inside)	26·33	—
On ring (outside)	21·95	19·14
Outside the ring	27·96	19·74

It will be observed that the percentage of water is almost uniformly lower in the soils taken from the ring-band than in those taken either within or outside it; and this generally holds good in the case of the subsoils as well as of the surface soils. The comparative dryness of the soil under the ring-band will in part be due to the greater evaporation incident to the greater activity of growth; but, in some cases, as in that of the Grove Paddock Ring, it is probably to be largely attributed to the action of the underground fungoid growth in giving to the soil, in some way not quite explicable, a power of resisting the free absorption of water, as if it were greasy, as already referred to.

In all the surface soils the nitrogen has been determined by combustion with soda-lime, and the carbon by combustion in oxygen; and in those from the Broadbalk Field and the Park Fairy Rings the nitrogen as nitric acid has also been determined. The subsoils have only been partially examined, and such determinations of nitrogen as have been made in them by the soda-lime method indicate that the variations in the amount are due to differences in the character of the subsoils, quite independent of the influences of the growth of the

fungi, and of the grasses succeeding them, which are the subjects of the present inquiry. Indeed, very numerous determinations of nitrogen in subsoils have shown that, with a low actual percentage, the variations in the amount in different samples are proportionally great, and obviously to a great extent unconnected with the special history of the plot from which the samples are taken. Moreover, so far as the total nitrogen and carbon are concerned, it seems probable that the influences of the fairy ring growth are, to a great extent, if not wholly, limited to the surface soils; and it will be seen that the results relating to them afford conclusive evidence on the points under inquiry.

In Table IV are given the percentages of nitrogen and carbon in the dry fine surface soils (that is excluding stones, roots, and water).

TABLE IV.—*Percentages of Nitrogen and Carbon in the Dry Fine Surface Soils.*

	Nitrogen.	Carbon.
Grove Paddock Fairy Ring Soils, May 19, 1874.		
Within the ring	0·262	3·06
On the ring	0·274	(2·72)*
Outside the ring	0·287	3·34
Broadbalk Field Fairy Ring Soils, June 18, 1877.		
Within the ring	0·271	2·38
On the ring	0·300	3·36
Just outside the ring	0·327	3·05
Quite outside the ring	0·303	3·52
Broadbalk Field Fairy Ring Soils, September 15, 1877.		
Within the ring	0·226	2·48
On the ring	0·244	2·60
Outside the ring	0·274	3·12

* In the Grove Paddock soils the carbon was not determined until some years after the collection, when the sample taken on the ring was found to have a high percentage of water, and a mouldy odour; it had doubtless lost carbon.

	Nitrogen.	Carbon.
The Park Fairy Ring Soils, September 19, 1877.		
Within the ring	0·222	2·88
On the ring (centre)	0·230	3·01
On the ring (outer edge)	0·276	3·40
Just outside the ring	0·259	3·31
The Park Fairy Ring Soils, April 25, 1878.		
Within the ring	0·253	3·12
On the ring (inner side).....	0·245	2·97
On the ring (outer side)	0·268	3·11
Outside the ring	0·269	3·44

Although, as has been said, all visible organic *débris* was carefully removed from the samples before nitrogen and carbon were determined in them, it will be readily understood that in the case of surface soils of grass land containing so much of such matter, it is extremely difficult to exclude the whole of it, whilst any irregularity in this respect will affect the amount of carbon more than that of the nitrogen; and a consideration of the results in detail leads to the conclusion that the carbon determinations are, from this cause, less trustworthy than those of the nitrogen. Still a glance at the Table (IV) shows that in each of the five series of samples the percentage of both nitrogen and carbon is much lower in the soils within the ring than outside it; that is to say, it is much lower where the action of the fungus and the growth and removal of the luxuriant crop of grass is past, than where the fungus has not yet been developed. In most cases where the action of the fungus is still in progress, the percentages of nitrogen and carbon are intermediate between those in the soils within and without the circle. The spread of the ring is in fact marked by a destruction of organic matter containing nitrogen and carbon.

It will be observed, however, that there are some apparent anomalies in the results, but on an examination of the circumstances of the experiments, these are sufficiently explained. Thus, the percentages of both nitrogen and carbon are much higher in the series of samples collected from the Broadbalk Field Fairy Ring in June, 1877, than in those collected from the same ring in the following September; and according to notes taken at the time, the sampling cylinder did not bring up so much soil in June as in September. In other words,

the samples taken in June comprised a larger proportion of the surface, and a smaller proportion of the subsoil, and hence the higher range in the percentage of nitrogen and carbon in them. Again, the percentages of both nitrogen and carbon are abnormally high in the sample from the Park Fairy Ring collected at the outer edge in September, 1877, and in the samples collected within the ring, and on the outer side of it, in April, 1878. In these cases also the cylinder brought up relatively small weights of soil, and hence the samples consisted in a relatively large proportion of surface soil, and showed accordingly higher percentages of nitrogen and carbon.

The general bearing of the results is unmistakably shown in the next table (V), in which, assuming each ring to be made up of the three divisions of "within," "on," and "outside," the results for each such division of the five different series of samples are brought together, and the mean taken. Thus, we have the mean of all the determinations on the samples taken within the ring, the mean of all those taken on the ring, and of all those taken outside it. At the foot of the table there is given the mean amount of nitrogen and carbon in the soils within, and on the ring, compared with that outside it taken as 100. There is also given the mean proportion of carbon to 1 of nitrogen in the soils taken at the different positions.

TABLE V.—*Mean Percentages of Nitrogen and Carbon in the Fine Dry Fairy Ring Soils.*

Description of ring.	Nitrogen per cent.			Carbon per cent.		
	Within the ring.	On the ring.	Outside the ring.	Within the ring.	On the ring.	Outside the ring.
Grove Paddock (May, 1874) ..	0·262	0·274	0·287	3·06	2·72	3·34
Broadbalk (June, 1877)	0·271	0·300	0·315	2·38	3·36	3·29
,, (September, 1877) ..	0·226	0·244	0·274	2·48	2·60	3·12
Park (September, 1877)	0·222	0·253	0·259	2·88	3·21	3·31
,, (April, 1878).....	0·253	0·257	0·269	3·12	3·04	3·44
Mean	0·247	0·266	0·281	2·78	2·99	3·30
N and C "outside" = 100	87·9	94·7	100	84·2	90·6	100
Carbon to 1 nitrogen.....	—	—	—	11·3	11·2	11·7

The results brought together in this way clearly bring to view the fact that in each of the five series of experiments the percentage of

nitrogen was the highest in the soil outside the ring, and the lowest in that within the ring. It was also in each case in intermediate amount in the soil on the ring. For the reasons already explained, the carbon results are not so trustworthy as those of the nitrogen. Still, the percentage of carbon is likewise in every case very much higher outside than within the ring; and it is, on the average, in intermediate amount on the ring. The general indications of the mean results may thus be safely relied upon. From these the conclusion already drawn from a study of the details becomes the more obvious, namely, that the growth of the fungus and the subsequent increased growth and removal of the associated herbage is accompanied by a considerable reduction in the amount of the organic nitrogen and carbon in the soil. Since prior to the growth of the fungus, that of the surrounding herbage was extremely restricted, and it became luxuriant only after the growth of the fungus, it cannot be doubted that it is primarily to its action that the reduction of the nitrogen and carbon in the soil is to be attributed. In other words, the fungi have taken up from the soil organic nitrogen and carbon that were not available to the previously established vegetation.

From the figures in the last line but one in the table, it is seen that reckoning the amount of nitrogen and carbon respectively outside the ring as 100, that of the carbon has been reduced in a greater proportion than that of the nitrogen, both on and within the ring. Accordingly the last line in the table shows that there was a higher proportion of carbon to nitrogen in the soil outside the ring than in that either on or within the ring. Calculation also shows that the proportion of carbon to that of the nitrogen lost by the soil is greater up to the stage of the active growth of the ring than afterwards, that is, the proportional loss of carbon is the greater under the more immediate influence of the growth of the fungus, and that of the nitrogen is the greater subsequently. Further, the relation of carbon to nitrogen is very much higher in the soil than it would be in the dry matter of the fungus. The action of the mycelium is therefore not only to reduce the carbon in a greater proportion than the nitrogen of the soil, but to do so in a much greater degree in proportion to the amount assimilated, a portion of the carbon being doubtless exhaled as carbonic acid. It is true that the proportion of carbon to nitrogen is much higher in the grasses which succeed the fungi than in the soil; but it is known that green-leaved plants generally, and grasses especially, derive most, if not all, of their carbon from the atmosphere.

Although the experiments do not supply data for exact calculation on the point, it may be stated, in general terms, that the mean results would represent a loss by the surface soil of several hundred pounds of nitrogen, and of several thousand pounds of carbon, per acre, by the

action of the fungus, and the subsequent luxuriant growth and removal of the grasses.

It was certainly to be expected that nitrates would be formed in considerable quantity on the decay of the fungus (whether in the stage of mycelium or of more advanced development), and possibly also on that of residual products of the action of the mycelium on the nitrogenous organic matter of the soil. It is quite in accordance with the supposition that nitrates are formed, that the band of grass following the track of the fungus should have the dark green colour which characterises it. It is, however, difficult to trace the formation of nitrates in meadow land, or at any rate to determine the quantity in which they are produced, as, owing to the amount and activity of the vegetation, they are for the most part taken up as soon as they are formed. Nevertheless, determinations of nitrates were attempted in the cases of the Broadbalk Field and of the Park Fairy Ring soils. The Crum-Frankland method was the one then in use, and was the one adopted. The soil extracts were purified by alcohol, but the chlorides were removed by silver. Under these circumstances the attack on the mercury was very feeble, and the nitrates present were undoubtedly under-estimated. The Broadbalk soils of the second collection have since been analysed by Schlösing's method, which is more accurate in the case of such extracts. The results of the determinations are given in Table VI below.

TABLE VI.—*Nitrogen as Nitrates per Million of Dry Fine Soil.*

	Crum-Frankland method.	Schlösing method.
Broadbalk Fairy Ring Soils, collected June 18, 1877.		
Within the ring	0·23	—
On the ring	0·92	—
Just outside the ring	0·43	—
Outside the ring	0·09	—
Broadbalk Fairy Ring Soils, collected September 15, 1877.		
Within the ring	1·31	1·03
On the ring	8·07	11·46
Outside the ring	1·10	2·44

	Crum-Frankland method.	Schlösing method.
The Park Fairy Ring Soils, collected September 19, 1877.		
Within the ring	trace	—
On the ring (centre)	0·46	—
On the ring (outer edge)	1·21	—
Just outside the ring	trace	—
The Park Fairy Ring Soils, collected April 25, 1878.		
Within the ring	0·17	—
On the ring (inner side)	1·21	—
On the ring (outer side)	none	—
Outside the ring	0·18	—

It will be seen that in the case of the second series of samples from the Broadbalk Field Ring, there was a very considerable amount of nitric acid in the soil of the ring-band. In all other cases the quantity, if any, was very small. It was, however, always more abundant in the soil of the ring-band than either within or without the circle.

In making the extracts of the surface soils for the determination of nitrates, it was observed that when mycelium was present, the watery extract was dark-coloured, and gave a bulky organic residue on evaporation. It is to be supposed, therefore, that some of the products of the decay of the mycelium, or of the action of the mycelium on the soil, will pass by drainage into the subsoil.

Some of the subsoils were examined for nitric acid, but scarcely more than a trace was found, excepting in the subsoil collected under the ring-band at the second sampling of the Broadbalk Field Ring soils, where the table shows the highest amount in the surface soils. Even here, however, the nitrogen as nitrates in the subsoil amounted to only 0·82 per million of the dry soil.

On a review of the whole of the results of our examinations of the soils of fairy rings, we think there can be no doubt that the source of the nitrogen of the fairy ring fungi is the organic nitrogen of the soil itself, which it assimilates, presumably, though not certainly, as organic nitrogen, and eventually deposits as manure which becomes available to the associated herbage. Further, the whole of the phenomena of the fairy rings, so far as the nitrogen is concerned, are thus explained without supposing any intervention of atmospheric nitrogen.

Evidence is still wanting to prove whether at all, or in what degree,

some green-leaved plants have a power of assimilating the organic nitrogen of the soil, such as is possessed by the fungi. That Leguminosæ, for example, will take up more nitrogen from an arable soil than Gramineæ would from the same soil is certain. In some cases part, if not the whole, of the increased assimilation of nitrogen by the Leguminosæ is doubtless due to the arrest of nitrates that would have been lost by drainage in the case of the growth of Gramineæ. In others, the evidence at command does not justify the conclusion that the whole of the increased amount can be so accounted for. Again, under the influence of potassium salts applied as manure, leguminous plants will take up a considerably increased amount of nitrogen, even from a poor arable soil; whilst under the same conditions a gramineous crop would not do so. This action is very marked when potash salts are applied to grass land. In this case, however, the percentage of nitrogen in the much richer surface soil is reduced in a degree easily determinable by the soda-lime method. The question arises, therefore, how far the increased amount of nitrogen taken up under these circumstances, is due to a liberation of soil-nitrogen independently of any direct action of the plant itself; or whether, under the influence of the potash supply, the plant acquires a character, or increased activity, of underground growth, by virtue of which it is enabled to take up the organic nitrogen of the soil in a manner, or in a degree, of which it is not otherwise capable? Some Leguminosæ, however, which have very deeply distributed roots, have the power of assimilating very large amounts of nitrogen over a given area, when growing on arable soil with the surface impoverished, and the subsoil naturally poor, so far as nitrogen is concerned.

ANNIVERSARY MEETING.

March 30th, 1883.

Dr. J. H. Gilbert, F.R.S., President, in the Chair.

The following Report was read by the President:—

According to the Bye-Laws, it is the duty of the President to present a report of the state of the Society at the Annual General Meeting of the Fellows. A glance at the Addresses of my predecessors shows that the obligation has been very variously interpreted, according to the special circumstances of the Society at the time, or to the special view of the President himself. There have been occasions when important questions affecting the interests of the Society had to be discussed—sometimes involving matters of internal working and management, at others the consideration of some new departure, with a view to more extended usefulness.

At present there are no such points requiring special notice. It is my duty rather to record steady progress in the attainment of the objects for which the Society was founded; and for myself, having been elected into the Society during its first Session, now within a few weeks of 42 years ago, it seems fitting that I should attempt to review the progress of the Society, in some important aspects, from the commencement of its existence up to the present time. I trust that such a review will not be without interest to the Fellows, and that it may even prove to be of some practical utility.

The Number of Fellows.—Obviously a very essential, though by no means the only necessary element, of the prosperity of a Society, the objects of which are defined to be—"The promotion of Chemistry and of those branches of Science immediately connected with it,"—is the number of Fellows it has attracted. I will, therefore, first call your attention to the progress of the Society in this respect.

Of the 25 gentlemen who met on February 23rd, 1841, for the purpose of taking into consideration the formation of a Chemical Society, the names of only two are still to be found in the list of our Fellows, Dr. Lyon Playfair, and Mr. Charles Heisch; and of the first Officers and Council, the name of not one is still there to be found. Indeed, of the 118 Members on the Register at the first Anniversary Meeting of the Society, held on March 30th, 1842, there remain only 12,

besides myself, who could now answer to the roll-call, namely, Professor Thomas Andrews, Mr. William Blythe, Dr. De la Rue, Mr. Charles Heisch, Mr. F. R. Hughes, Dr. G. D. Longstaff, Mr. Thomas Pearsall, Mr. J. Arthur Phillips, Dr. Lyon Playfair, Dr. E. Schunck, Mr. J. Denham Smith, and Dr. James Young.*

The following tabular statement shows the number of Ordinary Members or Fellows, of Associates, and of Honorary and Foreign Members, at the end of each period of five years, during the 40 years from 1841–2 to 1880–1 inclusive. It also shows, for comparison, the numbers for 1881–2, and for the year now closing, 1882–3:—

Five-year periods ending March 30.	Ordinary Members or Fellows.			Associates.	Honorary or Foreign Members.
	Total.	Increase.			
		Total.	Average per annum.		
1846	185	—	—	9	6
1851	229	44	8·8	2	20
1856	256	27	5·4	9	20
1861	342	86	17·2	10	30
1866	482	140	28·0	6	37
1871	582	100	20·0	3	34
1876	881	299	59·8	0	30
1881	1096	215	43·0	0	31
1881–2	1175	79	79·0	0	29
1882–3	1247	72	72·0	—	37

The following is a more detailed statement, in the usual form, of the Members for the past year 1882–3:—

Number of Fellows at the Anniversary, March 30th, 1882		1175
Since elected and paid admission fees		104
		1279
Removal on account of arrears	16	
Withdrawn	7	
Deceased	9	
	—	32
		1247

* W. R. Grove, Esq. (now Mr. Justice Grove), was present at the meeting for the formation of the Society, and was on the first Council, but is not now on the list of the Society.

Number of Foreign Members at the last Anniversary....	29
Since elected	9
	38
Deceased.....	1
Present number.....	37

Thus, we have lost by death 9 Fellows, and 1 Foreign Member. We have also lost 16 by removal on account of arrears, and 7 by withdrawal.

Notices of the Fellows lost by death will be given further on.

It will be seen that notwithstanding these losses, the total number of Fellows has increased by 72 since the last Anniversary Meeting, and our numbers stand higher than ever before. It has already been mentioned that, at the first Anniversary Meeting of the Society, there were 118 Ordinary Members on the Register, whilst now at the conclusion of its forty-second year there are 1247 Fellows on the list. In other words, our numbers have increased more than ten-fold from the first year to the last; and as the foregoing table shows, there has been, upon the whole, though with some fluctuations, an augmentary rate of increase. The record of the number of Associates is somewhat uncertain; but, notwithstanding the greatly increased number of Students of Chemistry, it has certainly declined in recent years, probably owing to preference for full Fellowship, as soon as the means of the student permit. At first the number of Honorary or Foreign Members was limited to 25; but with the great increase in the number of workers of eminence abroad, it was decided in 1860 to raise the limit to 40. This number was at one time filled up; but at the date of the last Anniversary Meeting it had become reduced by death to 29, and more recently to 28; and it will be in the recollection of the Fellows that only a few weeks ago the names of nine distinguished Foreign Chemists were added to the list, thus again bringing up the number to 37.

The important questions obviously suggest themselves—how far the work accomplished by the Society, and the advancement of Chemical knowledge in the country at large, are commensurate with the increase in its numbers. According to its Founders, the means to be adopted by the Society are—"the reading, discussion, and subsequent publication of Original Communications. Also the formation of a Chemical Library and Museum." What has been accomplished in regard to these several objects?

The number of papers presented to the Society:—This affords some measure of the activity of its Members, and of the work accomplished under its auspices, in the way of original investigation; and I think the

following summary will therefore not be without interest. It shows the total number of Papers read at the meetings of the Society, within each of the eight five-year periods of the first 40 years, and the average number per annum during each of those periods. It also shows the number of Discourses and Faraday Lectures that have been delivered; and at the foot of the table are given similar particulars for 1881–2, and for the year now closing, 1882–3:—

Five-year periods ending March 30.	Papers read.		Discourses delivered.	
	Total number.	Average per annum.	By Fellows.	Faraday Lectures.
1846	167	33·4	0	—
1851	209	41·8	0	—
1856	122	24·4	9	—
1861	140	28	17	—
1866	165	33	19	—
1871	201	40·2	17	1 (1869)
1876	264	52·8	14	2 (1872 & 1875)
1881	392	78·4	7	1 (1878)
1881–2	87	87	1	1 (1881)
1882–3	70	70	1	—

It is thus seen that after the first decade the number of papers presented to the Society decreased considerably; and in the Sessions 1854–55 and 1855–56, it only reached 17 and 18 respectively. In the Session of 1853–54 the first Discourse was delivered, by the late Professor Graham, it having been decided by the Council that—"In order to increase the interest of the meetings of the Society, certain meetings, not exceeding five in the year, shall, after the transaction of the ordinary business, be devoted to the delivery of Discourses on matters connected with the Progress of Chemistry, and which may be illustrated by experiment." Under this rule there have been 86 Discourses delivered during the period of nearly 30 years, from 1853 up to the present time. I may mention that on looking up these facts, I find that my own contribution to the series has been five; three of which were subsequently written and printed in the Journal as joint papers by Mr. Lawes and myself.*

In the third session after the adoption of the plan, as many as seven discourses were delivered; and in subsequent years as many as

* "On some Points in the Composition of Wheat Grain, its Products in the Mill, and Bread" (**10**, 1); "On the Sources of the Nitrogen of Vegetation, with special reference to the question whether Plants assimilate Free or Uncombined Nitrogen" (**16**, 100); "On the Composition, Value, and Utilisation of Town Sewage" (**19**, 80).

six, five, or four, have been given. In the five years ending 1861, 17; in the next five years, 19; in the next, 17, and in the next, 14 were given; but in the four years ending 1880, only 7; in 1880–81, not one; in 1881–82, only one; and in 1882–83, only one.

A glance at the list of the authors, and of the subjects of these Discourses, recalls to mind the great interest and value of many of them. But, however desirable it may be, in these days when Chemistry includes so many distinct branches of study, and most of the workers in it must of necessity be more or less specialists, to have the results obtained in other departments summarised and illustrated by those who have devoted special attention to them, it must nevertheless be accepted as a matter for congratulation that in recent years it has become less and less necessary to occupy the time of our ordinary meetings by such discourses. The legitimate object of our meetings is the reading and discussion of original communications, and supposing that a sufficient number of these is contributed, there is still, it seems to me, no reason why extra meetings should not be set apart for discourses, when subjects of general interest might with advantage be brought before the Fellows in that way. The fact is, that in the fourth decade of the Society's existence, the number of original communications presented to it greatly increased, and this marked increase in the number of papers read is coincident with the period of rapid increase in the numbers joining the Society. During the last four years the number of papers read have been 75, 113, 87, and 70 respectively; in each case, excepting the last, a larger number than in any previous year; and during these four years only three ordinary discourses have been delivered; not one having been given in the Session 1880–81, when the very large number of 113 papers was presented.

But during recent years, we have had five Faraday Lectures delivered, by Foreigners of marked distinction in their different spheres of labour. The inaugural address of the series was given by Dumas, on June 17th, 1869; and, although it was also much more, it was an eloquent tribute to the importance and influence of the labours of the great Philosopher in whose memory, and in whose honour, the Faraday Lectures were instituted. The second lecture was delivered by Cannizzaro, on May 30th, 1872, and was entitled "Considerations on some points of the Theoretic Teaching of Chemistry." The third was by Hofmann, on March 18th, 1875, "On the Life-work of Liebig in Experimental and Philosophic Chemistry." The fourth was by Wurtz, on November 13th, 1878, "On the Constitution of Matter in the Gaseous State." The fifth and last was given by Helmholtz on April 5th, 1881, "On the Modern Development of Faraday's Conception of Electricity."

The following is a list of the Papers read before the Society between March 30th, 1882, and March 30th, 1883:—

I. "On the Action of Acetyl Chloride on Fumaric Acid:" by W. H. Perkin.

II. "Some Arguments in Favour of the Prism-formula of Benzene:" by U. K. Dutt.

III. "Note on a Convenient Apparatus for the Liquefaction of Ammonia:" by J. Emerson Reynolds.

IV. "On the Transformation of Urea into Cyanamide:" by H. J. H. Fenton.

V. "On the Action of Haloïd Acids upon Hydrocyanic Acid:" by L. Claisen and F. E. Matthews.

VI. "On the Atomic Volume of Iodine:" by W. Ramsay.

VII. "On Molecular Volumes:" by W. Ramsay.

VIII. "On the Action of Acetone on Phenanthraquinone, both Alone and in the Presence of Ammonia:" by F. R. Japp and F. W. Streatfeild.

IX. "A Study of some of the Earth-metals contained in Samarskite:" by H. E. Roscoe and A. Schuster.

X. "On the Action of Thiophosphoryl Chloride upon Silver Nitrate:" by T. E. Thorpe and S. Dyson.

XI. "Note on the Action of Oxychloride of Sulphur on Silver Nitrate:" by T. E. Thorpe.

XII. "On the Behaviour of Zinc, Magnesium, and Iron as Reducing Agents with Acidulated Solutions of Ferric Salts:" by T. E. Thorpe.

XIII. "Experiments on the Action of Potassium-amalgam, Sulphuretted Hydrogen, and Potassium Hydrate respectively on Tetra- and Penta-thionates of Potassium:" by V. Lewes.

XIV. "On the Precipitation of Alums by Sodic Carbonate:" by E. J. Mills and R. L. Barr.

XV. "On Rotary Polarisation by Chemical Substances under Magnetic Influence:" by W. H. Perkin.

XVI. "On the Constitution of Amarine and Lophine:" by F. R. Japp and H. H. Robinson.

XVII. "On the Determination of Nitric Acid in Soils:" by R. Warington.

XVIII. "On a Spectroscopic Study of Chlorophyll:" by W. J. Russell and W. Lapraik.

XIX. "Notes on β-Naphthaquinone:" by C. E. Groves.

XX. "On some New Compounds of Brazilein and Hæmatein:" by J. J. Hummel and A. G. Perkin.

XXI. "On the Determination of Nitric Acid as Nitric Oxide by

means of its Reaction with Ferrous Salts." Part II: by R. Warington.

XXII. "On a New Process of Bleaching:" by J. J. Dobbie and J. Hutcheson.

XXIII. "Metallic Compounds containing Bivalent Hydrocarbon Radicals." Part III: by J. Sakurai.

XXIV. "On the Crystallisation from Supersaturated Solutions of certain Compound Salts:" by John M. Thomson and W. Popplewell Bloxam.

XXV. "On Oxypropyltoluidine:" by H. Foster Morley.

XXVI. "On some Halogen-compounds of Acetylene:" by R. T. Plimpton.

XXVII. "On Dihydroxybenzoic Acids and Iodosalicylic Acids:" by A. K. Miller.

XXVIII. "On Crystalline Molecular Compounds of Naphthalene and Benzene with Antimony Trichloride:" by Watson Smith and G. W. Davis.

XXIX. "Additional Evidence by an Analysis of the Quinoline Molecule that this Base belongs to the Aromatic Series of Organic Substances:" by Watson Smith and G. W. Davis.

XXX. "On Orcinol and some of the other Dihydroxytoluenes:" by H. C. Nevile and D. A. Winther.

XXXI. "On the Varying Quantities of Malt Albuminoïds extracted by Waters of Different Types:" by E. R. Moritz and A. Hartley.

XXXII. "On the Derivatives of Ethylene Chlorobromide:" by J. W. James.

XXXIII. "Contributions to the Chemistry of Tartaric and Citric Acids:" by the late Beaumont J. Grosjean.

XXXIV. "Contributions to the Chemistry of Bast Fibres:" by C. F. Cross and E. J. Bevan.

XXXV. "On the Oxidation of Cellulose:" by C. F. Cross and E. J. Bevan.

XXXVI. "On the Analysis of certain Vegetable Fibres:" by C. Webster.

XXXVII. "On the Constitution of some Bromine-derivatives of Naphthalene." Third Notice: by R. Meldola.

XXXVIII. "On the Constitution of Lophine:" by F. R. Japp.

XXXIX. "On the Condensation-products of Œnanthaldehyde." Part I: by W. H. Perkin, jun.

XL. "On the Condensation-products of Isobutyl Aldehyde:" by W. H. Perkin, jun.

XLI. "On the Condensation-products of Phenanthraquinone with Ethylic Acetoacetate:" by F. R. Japp and F. W. Streatfeild.

XLII. "On the Constitution of Lophine:" by H. E. Armstrong.

XLIII. "On the Constitution of Molecular Compounds. The Molecular Weight of Basic Ferric Sulphate:" by S. U. Pickering.

XLIV. "On the Chemistry of Hay and Ensilage:" by F. W. Toms.

XLV. "On certain Brominated Compounds obtained in the Manufacture of Bromine:" by S. Dyson.

XLVI. "Note on the Preparation of Diphenylene Ketone Oxide:" by W. H. Perkin.

XLVII. "On the Condensation-products of Œnanthaldehyde." Part II: by W. H. Perkin, jun.

XLVIII. "On the Behaviour of the Nitrogen of Coal during Destructive Distillation; with some Observations on the Estimation of Nitrogen in Coal and Coke:" by W. Foster.

XLIX. "On the Absorption of Weak Reagents by Cotton, Silk, and Wool:" by E. J. Mills and J. Takamine.

L. "The Alkaloïds of Nux Vomica. (No. 2.) On Brucine:" by W. A. Shenstone.

LI. "Preliminary Note on some Diazo-derivatives of Nitrobenzyl Cyanide:" by W. H. Perkin.

LII. "Researches on the Induline Group:" by O. N. Witt and E. G. P. Thomas.

LXIII. "On the Fluorine-compounds of Uranium:" by A. Smithells.

LIV. "On a New Method of Estimating the Halogens in Volatile Organic Compounds:" by R. T. Plimpton and E. E. Graves.

LV. "On a Modified Liebig's Condenser:" by W. A. Shenstone.

LVI. "On two New Aluminous Mineral Species, Evigtokite and Liskeardite:" by W. Flight.

LVII. "On the Volume-alteration attending the Mixture of Salt Solutions:" by W. W. J. Nicol.

LVIII. "On some Derivatives of Fluorene:" by W. R. E. Hodgkinson and F. E. Matthews.

LIX. "On the Action of Chlorine on certain Metals:" by R. Cowper.

LX. "Some Notes on Hydrated Ferric Oxide and its Behaviour with Hydrogen Sulphide:" by L. T. Wright.

LXI. "On Alphacyanonaphthalene-sulphonic Acid:" by U. K. Dutt.

LXII. "On some Derivatives of Diphenylene Ketone Oxide:" by A. G. Perkin.

LXIII. "On α-Ethylvalerolactone, α-Ethyl β-Methylvalerolactone, and on a Remarkable Decomposition of β-Ethylacetosuccinic Ether:" by S. Young.

LXIV. "On some Derivatives of the Isomeric $C_{10}H_{14}O$ Phenols:" by H. E. Armstrong and E. H. Rennie.

LXV. "On some Chemico-microscopical Researches on the Cell-contents of certain Plants:" by A. B. Griffiths.

LXVI. "On the Phenates of Amido-bases:" by R. S. Dale and C. Schorlemmer.

LXVII. "On some Condensation-products of Aldehydes with Acetoacetic Ether and with Substituted Acetoacetic Ethers:" by F. C. Matthews.

LXVIII. "Contributions to the Chemistry of Fairy Rings:" by Sir J. B. Lawes, J. H. Gilbert, and R. Warington.

LXIX. "On Lines of No Chemical Change:" by E. J. Mills and W. McD. Mackey.

LXX. "On Homologous Spectra:" by W. N. Hartley.

There have thus been only 70 papers read before the Society in the past year, against 87, 113, and 75, respectively, in the three preceding years; but prior to these years, only once, namely, in 1876–7, was there as high a number as in the year just passed. Of the 70 papers that have been read, rather more than one-half have been in the domain of Organic Chemistry, the remainder having reference to a wide range of subjects. Although, of necessity, investigations in Organic Chemistry, as indeed in other branches, involve much special detail, yet it cannot fail to be recognised that there is more and more of tendency to classification, and so to relieve the record of results of the character of the mere enumeration of isolated facts. The number of instances of the production in the laboratory of bodies formerly known only as products of vegetable or animal life, is also constantly increasing. Coincidently with these advances we find, not only in the original papers, but also in the systematic works, of both Vegetable and Animal Physiologists, much more of definiteness and certainty in the chemical explanation of the processes of the living organism. This is surely a very essential direction of advance in Organic Chemistry.

There has also been one Discourse delivered, by Professor Dewar—"On the Recent Development of the Theory of Dissociation." Dissociation was defined to be decomposition under such conditions—that the products of the reaction remain within the sphere of chemical action, and that the process is reversible, in the thermo-dynamic sense of the term. Attention was particularly called to the great accumulation of experimental evidence on the subject since the date of the

Lecturer's previous discourse (1874). Further, the mathematician had rendered great service to the chemist by systematising and classifying the phenomena. The phenomena of dissociation were illustrated by numerous experiments.

The Journal.—Reference will be made further on to the greatly increased space devoted in the Journal, in recent years, both to the Transactions, recording the work of our own Society, and to the Abstracts, indicating the activity of chemical research in other countries as well as our own. As showing the greatly increased circulation of our Journal, it may be of interest to state that, in 1863, when the new Series was commenced, the number printed was raised from 600 to 750; in 1868 to 850; in 1871 to 1500; in 1881 to 1750; whilst at the present time 1775 copies are printed. Of these between 1200 and 1300 are distributed to Fellows of the Society: and of the Journal of the present year (1883), 242 copies had been sold up to March 15; the distribution being approximately as follows:—At home, 70; to America, 70; to Germany, 40; to other parts of the continent of Europe, and to India, 60. Here I may mention in passing that, in a recent tour in America, I found our Journal was taken, and much appreciated, in most of the Institutions I visited.

The Library and Museum.—According to our Charter, the formation of a "Library of Scientific Works, and also a Museum of Chemical Preparations and Standard Instruments" are among the objects of the Society.

I am informed that a commencement was made many years ago in the formation of a Museum of Chemical Preparations; and it is recorded in the Journal that a number of specimens were contributed from the Great Exhibition of 1851. It seems, however, that the collection was not deemed to be of sufficient importance and value for maintenance and extension, and that it was eventually distributed; the specimens received from private individuals being returned to the donors, and others being sold. I have not found any record of the matter in the Journal; and I am not prepared to advise that another attempt should be made to form a chemical museum. But I may mention that it has been suggested to me as desirable that the Society should possess such a collection, and that, as a nucleus, the authors of papers on new compounds should be requested to present specimens to the Society.

Of the Library, a much more favourable account can be given. The last Catalogue of the Library was printed in 1873; and the Council have decided, on the recommendation of the Library Committee, that a new Catalogue, arranged in order of subjects, shall be prepared, printed, and issued to the Fellows, as soon as possible. The total number of volumes catalogued in 1873 was 3540, and there have

since been added to the Library 3260 volumes, making in all, at the present time, 6800 volumes. During the same period of about ten years, the number of pamphlets has been increased from 540 to 840.

The following is a more detailed statement of the previous and present contents of the Library, as kindly furnished to me by the Librarian:—

I. *Number of Systematic Works.*

Subjects.	1873.	Since added.	1883.
Physics	147	108	255
General Chemistry	170	86	256
Inorganic	23	26	49
Organic	27	31	58
Physiological	27	60	87
Vegetable Physiology and Agriculture	33	77	110
Analytical	37	128	165
Technical	122	234	356
Mineralogy and Geology	46	57	103
Meteorology	7	9	16
Biography	5	3	8
Miscellaneous	11	22	33
Dictionaries	8	15	23
	663	856	1519

II. *Number of Volumes.*

Volumes of systematic works in 1883	2600
„ Journals in 1883	3600
„ Duplicate Journals for circulation	600
Total number of volumes	6800
Catalogued in 1873	3540
Added 1873 to 1883	3260

The number of Pamphlets in the Library is as follows:—

In 1873	540
Since added	220
Total	760

Thus the Library has been nearly doubled in the last ten years, and our shelves are very nearly full. There can be no question that the provision of a good Library of Scientific Works and Journals is one

of the most important objects to which the funds of the Society can be devoted; and it is desirable that the Fellows should make themselves acquainted with the Rules for the use of the Library at Burlington House, and also for the circulation of Works and Journals, which are now of a very liberal and practical character, offering great facilities for study and for reference.

The Research Fund.—The Treasurer will present a detailed statement of the accounts of this Fund for the past year. It may be well, however, to give, in this place, a brief notice of the history and general condition of the Fund. In 1872, Mr. T. Hyde Hills offered a donation of £10, and to continue a like donation for several years, under certain conditions as to co-operation, with a view to the institution of a small special fund to be expended in money grants to investigators; but this proposal did not at the time meet with sufficient response. In 1876, one of the original members of the Society, Dr. G. D. Longstaff, offered the sum of £1000 towards the establishment of a permanent fund for the furtherance of research, provided a like sum were subscribed, and the £2000 invested for the purpose. It is not a condition that the fund should necessarily be expended exclusively in the form of money grants to investigators, but that it should be applied in any ways the Council may from time to time consider the most conducive to the advancement of Chemical Science. The conditions as to further subscriptions were very soon fulfilled, as the following tabular statement will show:—

Years.	Donations and subscriptions.	Investments.	Dividends.	Grants.
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
1876*.....	1000 0 0	1000 0 0	—	—
1876–7.....	2333 13 0	2050 0 0	—	—
1877–8.....	986 19 0	919 12 6	121 11 11	245 0 0
1878–9.....	227 6 0	—	138 19 11	250 0 0
1879–80.....	273 11 0	102 17 6	141 2 6	495 0 0
1880–1.....	257 7 0	313 2 6	141 12 0	111 0 0
1881–2.....	142 5 0	—	171 12 5	100 0 0
1882–3.....	120 1 0	212 0 0	137 3 5	220 0 0
Totals	5341 2 0	4597 12 6	852 2 2	1421 0 0

It will be understood that it is no part of my purpose to present a balance sheet of the Research Fund, which the foregoing statement obviously does not do. I may mention, however, that up to the present time the expenses of the administration of the Fund have

* Dr. Longstaff's original donation.

amounted to less than £10. It will be seen that the amount disbursed as grants considerably exceeds the dividends on the sums invested, nearly, £600 having been appropriated from the subscriptions. Still, the amount invested remains at about £4600. Although it is obviously desirable that a sufficiently large sum should remain invested to yield an income available for future demands, it would appear that the Fund could without detriment meet larger claims than it has recently been called upon to do, provided it seemed that researches of sufficient importance and promise could appropriately be so aided.

The Finances of the Society.—Here, again, it is no part of my intention to present anything in the way of a balance-sheet, my only object being to give a general view of the progress and position of the Society in the matter of finance in some aspects of interest.

Below is given the average annual income from various sources, over each five-yearly period of the first 40 years of the Society's existence; also the average annual expenditure over the same periods, on the Journal and the Library accounts, each separately, and in other ways collectively.

Income.

Five-year periods ending March 30th.	Entrance fees, subscriptions, compositions, donations.	Dividends.	Miscellaneous.	Legacies.	Total.
	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
1846.....	183 5 0	—	—	—	183 5 0
1851.....	360 12 11	6 2 4	36 15 9	—	403 11 0
1856.....	333 1 2	10 13 10	80 9 4	—	424 4 4
1861.....	550 16 0	8 9 8	39 12 10	—	598 18 6
1866.....	736 0 11	24 16 3	26 13 5	—	787 10 7
1871.....	1024 15 5	72 5 11	57 2 5	—	1154 3 9
1876.....	1758 1 11	97 12 9	237 19 5	—	2093 14 1
1881.....	2047 15 7	194 6 5	360 1 10	568 1 0	3170 4 10
1881–2....	2396 1 6	231 7 3	407 8 6	—	3034 17 3
1882–3....	2444 3 6	245 10 1	383 11 6	—	3073 5 1

Expenditure.

Five-year periods.	Journal.			Library.			Miscellaneous.			Investments.			Total.		
	£	*s.*	*d.*	£	*s.*	*d.*	£	*s.*	*d.*	£	*s.*	*d.*	£	*s.*	*d.*
1846.....	45	11	4	10	3	11	39	1	7	—			94	16	10
1851.....	187	15	5	18	3	4	133	14	5	99	12	3	439	5	5
1856.....	179	13	1	32	3	2	245	19	0	—			457	15	3
1861.....	219	8	1	49	14	1	168	19	6	65	17	3	503	18	11
1866.....	352	2	4	73	17	6	177	4	10	145	14	6	748	19	2
1871.....	409	14	6	89	12	9	230	13	6	310	0	6	1040	1	3
1876.....	1189	13	8	149	18	11	650	14	8	93	15	0	2084	2	3
1881.....	1654	9	3	330	2	5	508	2	11	712	13	11	3205	8	6
1881-2....	1733	11	10	233	4	11	526	9	7	324	7	6	2817	13	10
1882-3....	1944	13	3	307	9	10	517	5	0	530	0	0	3299	8	1

Thus our income from entrance fees, subscriptions, compositions, and donations, has increased from an average of under £200 over the first five years, to over £2000 over the last five years of the first 40; and in the past year it amounted to over £2400. Our annual income from dividends, which was nothing in the first five years, now amounts to nearly £250; whilst miscellaneous items, including the sale of the Journal, &c., amount to nearly £400. We have also received during the eighth five years a sum of £2840 5*s.* in three legacies (from Mr. Dirck £840 5*s.*, from Mr. Lambert £1000, and from Mr. Ellis £1000), giving the average per annum over the period of £568 1*s.* shown in the table.

As to the expenditure: on the important item of the Journal it averaged little more than £45 per annum over the first five years, more than £1650 over the last five years, and in the past year it was not far short of £2000. This expenditure increased very rapidly during the last two five-yearly periods. From the amounts of cost given, there have to be deducted the proceeds of the sale of the Journal. But this largely increased and increasing item of our expenditure must be looked upon with great satisfaction, as indicating very important work accomplished, and widely spreading usefulness.

The expenditure on the Library is on a very much smaller scale than that on the Journal, but it also has very considerably increased. The average annual expenditure on the Library was little over £10 over the first five years, and it exceeded £330 over the eighth five years; but it has been rather less since. This increase must also be considered as a source of gratification to the Fellows, as it speaks of much enhanced facilities for study.

Of the other items of expenditure, I have nothing to say, excepting

that they show a constantly-increasing activity in our proceedings. One more item of satisfaction may be noted, namely, that, notwithstanding our greatly increased expenditure in the maintenance and furtherance of the objects of the Society, we are still able gradually to add to our store of invested capital.

As bearing upon the progress of the Society in the past, and its probable prospects in the future, it was my intention to give, as far as possible, a statistical view of the vast development of chemical education in this country, since the date of its foundation; but although I have been kindly provided with some material for the purpose, the only result has been that I have found it quite impracticable, with the time at my command, and with due regard to the proper limits of my address, to treat the subject in that way. I can only direct attention, in general terms, to the great advances that have been made; and it is the less necessary to do more, since the majority of the Fellows are well aware of the facilities now at the command of the chemical student.

By way of illustration of the change which has taken place, I may mention that my own first session in a chemical laboratory was in 1838–9, that is, a few years before the foundation of this Society, under the late Professor Thomas Thomson, of Glasgow. There were only three laboratory students besides myself, one of whom, the late Dr. Stenhouse, is well known to the Fellows of this Society by his researches; and I had the advantage of meeting him again in the Giessen Laboratory in 1840. There was, I believe, at that time no systematic course of training in this country, first in qualitative, and then in quantitative work. For myself, after a little instruction in the use of the balance, I was at once set to analyse the minerals Prehnite and Stilbite, and was referred to books for method. The Professor was, however, always ready to give kind attention and assistance to the student when required. Dr. James Young informs me that what is known as a "practical class" had already before that time been established at the Andersonian College, Glasgow, by the late Professor Graham; and that he established one at University College, London, on going there about the year 1837. Such a class was in active work when I was at University College in the Sessions of 1839–40, and 1840–1. There can be no doubt, however, that the training for research was much less systematic then than it has been since; though a glance at the list of the early Fellows of this Society is sufficient to show that good chemists were nevertheless so trained.

It was at the anniversary meeting of the Society in March, 1847, that the President, Professor Graham, referred to the recent establishment in London, of chemical laboratories, expressly designed to further

the prosecution of original research, adding that—"The new laboratories of the College of Chemistry, and of the two older Colleges of the London University, now offer facilities for practical instruction and research not surpassed, we believe, in any foreign school. They already exhibit their efficiency, and claim our grateful recognition in the persons of new and promising contributors to our Memoirs."

Up to this time, it had been alleged that Organic Chemistry was neglected in these islands; and certainly from about the date just quoted, research in that department received a great impetus in this country. At the same time, it is only due to say that prior to the establishment of these new laboratories, the records of our Society bear testimony to the activity of a few of our countrymen in such research. Among these the name of Stenhouse has the most prominent place, but the names of Schunck, W. Gregory, and J. Blyth should not be omitted. Whilst referring to the earlier volumes issued by the Society, I may perhaps mention in passing, though the service rendered may not be much more than that of the organ-blower to the performer, that the third paper in our "Memoirs" (1841), is a translation by myself of Redtenbacher and Liebig's paper—"On the Atomic Weight of Carbon"—a fact which I had entirely forgotten until looking up the particulars above alluded to.

Not only have the facilities for training in, and for the prosecution of, research, been very greatly augmented in the three Institutions referred to by Graham, since that date, but such facilities have long been provided in connection with numerous other Schools in the Metropolis. Our two older Universities, Oxford and Cambridge, have also their well-appointed laboratories and schools of research. Very great advances have been made in the same direction in connection with the Scotch Universities, as well as with both the older and the newer Colleges in Ireland. To add to this, we have chemical schools of rapidly increasing influence in almost every important centre of population or industry in England. Thus, we have the Victoria University, with its active and efficient Schools of Chemistry at Manchester and Leeds, from both of which our Society receives valuable communications. Then, at Bristol, at Birmingham, at Newcastle, at Sheffield, and at Nottingham, there are very promising institutions, in which the Chemical Department is conducted by Fellows of this Society, well known by their original work. Moreover, almost every Public School now recognises the necessity of some training in chemistry. Besides all this, we have a rapidly developing system of instruction in the technical applications of chemistry, both by lectures and laboratory practice. As prominent examples of institutions specially designed to provide such instruction, may be mentioned the School of Mines; the School of Technical Chemistry in connection with Ander-

son's College, Glasgow, founded and endowed by Dr. James Young*; and the Schools of Chemistry already established, and to be established, under the auspices of the City and Guilds of London Institute for the Advancement of Technical Education.

With this great development in the past, and all that it promises in the future, there is surely every reason for believing that our Society must increase, both in the number of Fellows, and in the number and value of the papers communicated to it. There have, it is true, been two offshoots from the Society during the last few years, viz., the Institute of Chemistry, representing professional chemists as such, and the Society of Chemical Industry, each with its meetings and its publications. But, so far as I know, neither has prospered at the expense of the number of, or of the work accomplished by, our own body. It is true that, according to the terms of our Charter, one object of our Society is, "the general advancement of chemical science, as intimately connected with the prosperity of the manufactures of the United Kingdom, many of which mainly depend on their application of chemical principles and discoveries for their beneficial development, and for a more extended and economical application of the industrial resources and sanitary condition of the community." Yet, it may be a question whether the valuable papers which have been presented to and published by the Society of Chemical Industry would have reached our own Society at all, or whether, on the other hand, they have not had their origin altogether under the auspices of the new Society, and are, so far, a pure gain rather than a transference of usefully directed energy. Nor must we overlook the fact, that the number of papers read at our own meetings has, upon the whole, steadily increased in recent years, notwithstanding the large number of chemical papers presented to the Royal Society. In fact, the experience of that Society, like that of our own so far, goes to show that any loss of contributions that may arise from the establishment of departmental Scientific Societies is amply compensated by the increased activity of research.

In this connection, mention should be made of the fact that a considerable number of papers have been received and published by the Society, recording the results of investigations made by the aid of grants from the Research Fund of our Society, established in 1876. Some of the results of the researches so made have, however, been published elsewhere; but, on the other hand, we have received communications resulting from investigations conducted with aid from the Government Research Fund administered by the Royal Society.

A further measure of the increasing activity of research in this

* It is understood that in building, equipment, and endowment, Dr. Young has expended about £20,000.

country is the greatly increased space devoted in our annual volume to the "Proceedings" and "Transactions." Thus the average annual number of pages so devoted during each five-yearly period from the commencement to 1881 inclusive has been 187, 344, 170, 290, 460, 458, 363, and 673, falling however last year, 1882, to only 438.

Of the activity of chemical research on the Continent of Europe little need be said. Many of our Fellows have studied in Continental laboratories, and those who have not are able to form a very clear idea of the variety, extent, and value, of the work accomplished, from the Abstracts published monthly in our Journal. As indicating the growing activity of chemical research generally, it may be mentioned that the number of Abstracts and Titles of Papers given in our Journal was more than 1600 in 1878, nearly 1800 in 1879, and more than 1800 in 1880. In the first year, 1870–1, they occupied 1015 pages, over the next five years the average was 969 pages, over the next five years 1077, and in the last volume, that for 1882, 1340 pages, arranged under the headings of—

General and Physical Chemistry;
Inorganic Chemistry;
Mineralogical Chemistry;
Organic Chemistry;
Physiological Chemistry;
Chemistry of Vegetable Physiology and Agriculture;
Analytical Chemistry;
Technical Chemistry.

Of the extent of the arrangements for chemical education and chemical research on the American continent, much less is known in this country. It happens that I made a rather extended, but much too hurried a tour in America last autumn; and mentioning some of the facts I had there observed to officers of this Society, I have been asked if I could not give some account of the condition of things in my address.

I may premise that a special object of my journey was to communicate a joint paper by Sir J. B. Lawes and myself at the meeting of the American Association for the Advancement of Science held at Montreal, in August. I then visited the Canadian Province of Manitoba, and some of the Central and Western States of the Union, to acquire information as to the extent, and especially as to the fertility, of the vast areas of newly settled, or as yet unsettled lands, to which we look, not only as an outlet for our surplus European populations, but as a source of supply of a material amount of the food of those who remain behind.

Naturally, however, I took the opportunity of visiting Schools of

Chemistry whenever I was able to do so. I was struck with the provision already made in some States of the Union, that were hardly if at all settled when this Society was established, and which have only been within a comparatively few years brought into the Union as States. For example, and only as example, I may mention that in the State of Minnesota, only brought into the Union as a State in 1858, there is, at Minneapolis, the University of Minnesota, with both Professors and Students of both sexes; and there I found a laboratory with working room for 64 students, under the direction of Professor Dodge, who was educated in laboratories on the Continent of Europe, and in England. Again, in California, which was brought into the Union as a State only in 1850, I found at Berkeley, a few miles from San Francisco, the University of California, with its several laboratories for General Chemistry, and its laboratory for Agricultural Chemistry. The Professor of Chemistry, Dr. Rising, had studied in European laboratories, and the Professor of Agricultural Chemistry, Dr. Hilgard, was engaged in investigations on soils.

Of what is doing in the Eastern, and some of the Southern States much more is known. But feeling that my own personal observations had been far too limited in extent, and were made far too hurriedly to enable me to give an account of any value, I applied to Sir Alexander Galt, the High Commissioner for Canada, and to His Excellency Mr. Lowell, the American Minister in London, for any further information that might be available. From both I have received the most courteous attention and most substantial aid. I am also much indebted to Mr. Hoppin, the Secretary of Legation of the United States, to the Hon. John Eaton, Commissioner of Education at Washington, and to Mr. Colmer, the Secretary to the High Commissioner for Canada, for their very cordial co-operation in the matter. Indeed, the records supplied to me are far more copious than I have either time or space at all adequately to summarise. Still, the brief notice I am able to give of the progress of Chemistry on the other side of the Atlantic, will, I trust, be not altogether without interest, and will at any rate serve the purpose of directing attention to the subject, and to sources of further information.

Referring first to Canada, any information respecting the provision for scientific teaching there cannot fail to be of special interest at the present time, in view of the proposed visit of the British Association for the Advancement of Science to Montreal next year. No printed official reports on the subject have, however, been furnished to me, and whether such exist I am not aware. The facts I am able to give are from returns in answer to a form of questions I submitted, copies of which were kindly forwarded to the proper authorities for reply.

At *Ottawa*, the Capital of the Dominion of Canada, there is the

University of Ottawa, established in 1866, with laboratory accommodation for 20 students.

At *Montreal*, in the *Province of Quebec*, there is the McGill University, chartered in 1821, with its Faculties of Arts, Applied Science, Medicine, and Law. Chemistry is taught in Arts and Applied Science by Dr. B. J. Harrington, and in Medicine and Applied Science by Dr. G. P. Girdwood. There is laboratory accommodation for 25 Arts and Applied Science Students, and for 40 Medical Students. In Arts and Applied Science 60 Students take chemistry, of whom about half work in the laboratory, chiefly the more advanced. In Medicine, at present 116 are taking chemistry, of whom again nearly half work in the laboratory.

At *Quebec* itself, there is the Laval University, including a Medical Faculty, but the Faculty of Arts is not yet organised. There is a spacious chemical laboratory, with complete apparatus, &c., but no further information is given.

In the Province of *Ontario* there are numerous Schools of Chemistry.

At *Toronto*, there are University College and the School of Practical Science combined. These institutions include the various departments of general, medical, and technical instruction. The Professor of Chemistry is Dr. Pike, a Fellow of this Society. There is laboratory accommodation for 60 students, and there are a lecture and a laboratory assistant. There is also the School of Medicine, established in 1843, with laboratory accommodation for 24 students, and there is Trinity College, established in 1852, with laboratory accommodation for 30 students.

At *Kingston*, there is Queen's University College, established in 1840, where there is provision for 12 laboratory students ; and there is the Royal Military College with accommodation for 12, which it is proposed to increase to 25.

At *Cobourg*, there is the Victoria University, established in 1841, with a Professor and Assistant Professor of Chemistry, and one assistant ; and there is laboratory accommodation for 30 students.

At *Belleville*, there is the Albert College, established in 1857, with a Professor of Chemistry, but what laboratory accommodation is not stated.

At *London* (Ontario), there is the Western University, chiefly a Medical School, established in 1882. There is at present laboratory accommodation for 25 students, which it is intended to raise to 50.

In *Nova Scotia*, there is the Dalhousie College and University, at Halifax, with its Academic, Scientific, and Medical departments, and provision for 13 laboratory students.

In *New Brunswick*, the College of New Brunswick was founded at Fredericton in 1800 ; in 1828 it was, by Royal Charter, entitled King's

College, Fredericton; and in 1860, by amended Charter, the University of New Brunswick. Laboratory accommodation is provided for six students.

At *Winnipeg*, in the very recently and as yet only partially settled Province of Manitoba, I am informed there is already provision made for the teaching of chemistry, and that there is laboratory accommodation for six students.

In *Prince Edward Island* there is provision for elementary instruction in chemistry in some of the higher schools; but none other is provided. Nor, so far as my information goes, is there as yet any provision made for the teaching of chemistry in the far distant and recently settled province of British Columbia. But as I believe the Government have reserved lands along the line of the Canadian Pacific Railway to serve as endowment for educational purposes, it is to be expected that a knowledge of chemistry, the application of which must have such a direct influence on the economic development of the country, will in time be furnished by aid from this source.

Next, referring to the United States, although I travelled over about 11,000 miles on the American Continent, I crossed the borders of little more than half the 38 States of the Union; and was able to visit the scientific institutions of only a few of these. I have, however, been supplied with official information, both printed and written, as to the provision for teaching chemistry in nearly all the States. In almost every State there is provision made in Universities or Colleges, and also in secondary and High Schools and Academies.

I need only make reference to the institutions of the higher order. In many of the States, especially the more recently settled ones, the education in chemistry is in connection with an "Agricultural," a "Mechanical," an "Industrial," a "Mining," a "Medical," or a general "Technical" department. In such cases, therefore, the object is directly practical; and the training is little calculated to lead the student into the lines of original research. In almost every case, however, provision is made for work in the laboratory, as well as for instruction by lectures; and an original investigation is sometimes required to graduate.

I have already referred to the provision made at the Universities of Minnesota and California, and I will give one or two more examples of institutions where arrangements of the kind are comparatively recent.

Thus, it is stated that in the *Illinois Industrial University* at Urbana, there is laboratory accommodation for from 200 to 300 students; and the full course for a degree in the school of chemistry includes instruction in chemistry as follows:—First year, chemistry with laboratory practice (qualitative analysis), organic chemistry, and quantitative analysis. Second year, agricultural chemistry, with analysis; pre-

paration of salts, acids, &c. Third year, ultimate organic analysis, blowpipe analysis, assaying, both dry and humid, photography, including the preparation of photographic chemicals. Fourth year, gas analysis, analysis of waters, toxicology, including the microchemistry of poisons, original research, and thesis. The chemical portions of the course are, however, variable, according to the future objects of the student.

As another example, the *Iowa State Agricultural College* may be taken. It is stated that there is laboratory accommodation for 100 students, each provided with gas, sink, &c., and those engaged on quantitative work, with filter-pumps. The instruction is largely by lectures; but the beginner spends two afternoons a week in the laboratory, at qualitative analysis; quantitative analysis next follows; then volumetric methods, food analysis, and instruction in organic chemistry, both practical and theoretical. In the senior year, lectures twice a week on agricultural chemistry, lectures on food, the value and the use of the proteïn bodies, carbohydrates, fats, salts, &c. Special work is in the line of soil analysis, and the analysis of corn and grasses.

The foregoing examples may, I think, be taken as giving a fair idea of the character of the arrangements for the teaching of chemistry in the State or other institutions of the higher class, in many of the Central, Southern, and Western States; but further information will be found in the official document, entitled "Circulars of Information of the Bureau of Education No. 6, 1880, Washington."

I must go a little more into detail in reference to some of the institutions in the Eastern and South-Eastern States.

The Sheffield Scientific School, Yale College, New Haven, Connecticut.—In the history of American Science, Yale has played a very prominent part. Previous to 1770, chemistry was taught by tutors, and only became a regular subject of instruction about the beginning of the present century, the elder Silliman being appointed professor in 1802, a position which he held for nearly 50 years. In 1818 Professor Silliman issued the first number of the *American Journal of Science*, which still flourishes, and is well and favourably known in this country. In 1846 two professors, J. P. Norton, and B. Silliman, Junior, were appointed. This commenced the Scientific School, which, by the gifts of Mr. Sheffield, in 1859 and later, was placed upon a permanent basis. In 1863, the school received the National Land Grant, and became "The College of Agriculture and Mechanic Arts of Connecticut." Professor S. W. Johnson has now for many years been at Yale, and on my visit there he kindly devoted himself to showing me all that was likely specially to interest me in the arrangements.

The Laboratories are :—

1. A laboratory for elementary chemistry for the freshman class.
2. A laboratory for qualitative analytical chemistry.
3. A laboratory for quantitative analytical chemistry and various chemical investigations.
4. A laboratory for physiological chemistry.

An additional room in the basement is fitted up with furnaces and apparatus for assaying of ores in the dry way. Further, the determination of minerals is carried on in a laboratory arranged specially for that purpose.

The laboratories are well fitted, but some of them are too small. At present 41 students work in the laboratories for analytical and physiological chemistry ;—30 undergraduates in the courses of chemistry, biology, and agriculture, eight graduates, and three special students. They work four hours a day, under the supervision of four instructors. The laboratory accommodation is about to be increased.

Students enter the school with various objects; with a view to agriculture, metallurgy, mining engineering, pharmacy, or other professions. An increasing number study chemistry as a pure science, deciding to make it a permanent pursuit, in the expectation of becoming instructors, or analytical chemists, for which the liberal amount of time devoted to laboratory practice in chemical analysis is specially advantageous.

The Freshman receives preparatory instruction in chemistry. In the junior year the instruction is by text-books and recitations, with four hours a day in the laboratory five days a week, one being devoted to mineralogy. The work is partly experimental in organic chemistry—the synthetic preparation of organic compounds, &c. In the senior year also four hours a day are devoted to the laboratory. The student may gain experience in the assaying of ores, in the analysis of some particular class of products, or he may devote his time to original research. The facilities for graduate students are constantly increasing. The laboratories for analytical and physiological chemistry are open seven hours daily for their use. After suitable preparation, original investigation is encouraged. Work of this kind has proved to be a most valuable training, and has resulted in the production of some contributions to science of considerable value.

Harvard University, at Cambridge, Massachusetts.—At Harvard College, Josiah P. Cooke is the Professor of Chemistry and Mineralogy ; C. L. Jackson and H. B. Hill are Assistant Professors of Chemistry. There is also an Instructor, and there are three Assistants. Here I was fortunate enough to meet Professors Asa Gray, Horsford, J. P. Cooke, C. L. Jackson, Wolcott Gibbs, and others.

The laboratory accommodation consists of a qualitative laboratory with 100 desks; a quantitative laboratory with 24 desks; an organic chemistry laboratory with 12 desks; and a mineralogical laboratory for 24 students. There are a room of constant temperature for gas analysis, a furnace room, a balance room, and library, a larger and a smaller lecture room, and three private laboratories.

There is a summer course in chemistry for teachers of both sexes, which is largely attended. The subjects taught are: General chemistry, qualitative analysis, quantitative and organic analysis, the preparation of chemical substances, mineralogy, crystallography, blowpipe analysis. Every facility is given in the laboratory.

The teaching of chemistry in Harvard University dates from 1782, when Aaron Dexter was appointed Professor. He occupied the chair until 1816, and was succeeded by Professor John Gorham, who held it till 1827. In 1819, Dr. Gorham published the first systematic work on chemistry by an American author.

In 1847, the *Laurence Scientific School* was organised, and Professor E. N. Horsford inaugurated a system of laboratory instruction. In 1863, Professor Wolcott Gibbs succeeded Professor Horsford. Up to 1871, when the Chemical instruction consolidated with that of the College, and Dr. Gibbs became Professor of Physics, the school was the foremost in chemistry in the country.

In 1850 Dr. Cooke was elected Erving Professor in Harvard College. Laboratory instruction was first recognised as a part of the College course in 1859, when the present laboratory building was completed. Many researches in chemistry have been published from Harvard University.

Cornell University, at Ithica, State of New York.—Here I was very kindly received both by President White, and Professor Caldwell. C. A. Schæffer is Professor of General and Analytical Chemistry; G. C. Caldwell of Agricultural and Analytical Chemistry; C. H. Wing of Organic Chemistry; A. A. Breneman of Industrial Chemistry; and there are several assistants.

The laboratory accommodation is as follows: 1, the general laboratory for introductory and qualitative work; 2, a special laboratory for general quantitative analysis; 3, a special laboratory for agricultural and medical quantitative analysis; 4, a blowpipe room; 5, an assay room; 6, a room for spectroscopic and other optical work in chemistry; 7, a room for weighing and for the analysis of gases; 8, a reading room, well provided with chemical journals and other works of reference. Hydrogen and sulphydric acid are carried to the different rooms from generators. Richards' jet aspirator is used for water blast and filter-pumps, one of the latter being attached to every working table in the quantitative laboratories. These rooms are also

fitted with steam evaporating baths, drying closets, self-regulating air-baths at different temperatures, batteries for electrolytic determinations, and so forth. A new laboratory building was about to be occupied, including Museum, Library, Laboratories, Lecture rooms, &c., with the most recent appliances for chemical work.

University of Pennsylvania, at Philadelphia.—There are numerous schools of chemistry in Pennsylvania, but I can only refer to that of the University at Philadelphia. Dr. F. A. Genth, who kindly showed me the Laboratories, is the Professor of Chemistry and Mineralogy; G. A. König Assistant Professor and Instructor in Metallurgy and Technical Chemistry; S. P. Sadtler Assistant Professor and Instructor in General and Organic Chemistry; E. F. Smith Assistant in Analytical Chemistry. The laboratories are exceptionally fine, and fully equipped for all fields of chemical instruction. There is also a chemical museum. Numerous original investigations have been published by Professors Genth, Sadtler, and Smith. Chemistry has been taught here for more than a century in a limited way; but the present system of teaching was established in 1872.

There is also a very large Medical School in connection with the University. I had the good fortune to meet Dr. Wormley, the Professor of Chemistry and Toxicology, and Dr. J. Marshall, the Senior Assistant; there are also several other assistants. The laboratories of this department are very large and well appointed. There is already bench-room for 144 junior and 144 senior students to work at one time; and there is room for the fitting up of 72 places more in each of these laboratories. Thus there is at present laboratory accommodation for 288 students, which can be extended for 432.

College of New Jersey at Princeton, State of New Jersey.—It was here that the first regular professorship of chemistry was established in America. Dr. John McClean was appointed in 1795; and it was in his laboratory that the elder Professor Silliman first became acquainted with experimental chemistry. In physics, Princeton won distinction from the researches of the late Professor Joseph Henry, who was professor there prior to the organisation of the Smithsonian Institution at Washington. J. S. Schanck is now the Professor of Chemistry, and H. B. Cornwall, Professor of Analytical Chemistry and Mineralogy. General inorganic chemistry, blowpipe analysis, qualitative analysis, quantitative analysis, volumetric work, assaying, applied chemistry, and organic chemistry, are taught. Here I received every attention from Principal McCosh and Professor Cornwall.

University of Virginia, at Charlotteville.—Dr. J. W. Mallet, F.R.S., and also a Fellow of our Society, is the Professor of Chemistry; and Professor F. P. Dunnington has charge of the laboratory work. There is a course of general or scientific chemistry, and a course of

industrial or applied chemistry; also a short course in agricultural chemistry. The laboratory is specially built, and is capable of accommodating 50 students. There is a class of qualitative and a class of quantitative analyses. Students are strongly urged to undertake original research; and the result has been that a considerable number of original memoirs have been published from this laboratory. Special subjects are also taught, such as assaying, technological research, &c.

Johns Hopkins University, at Baltimore.—On the occasion of my visit new laboratories were in course of construction, and Professor Remsen kindly explained to me the existing and proposed arrangements as far as possible. Dr. Morse is Assistant Professor; there are several assistants; and Professor J. W. Mallet, of the University of Virginia, lectures upon Technological Chemistry. Courses are given in general chemistry, laboratory work, organic chemistry, analytical chemistry, the history of chemistry, on waste products of chemical manufacture, and the chief branches of chemical industry. The reading and discussion of current chemical journals are also a feature in the training. Professor Remsen, with the assistance of several other chemists, edits the "*American Chemical Journal*," in which the results of numerous researches made at this University, and elsewhere, are published. Research is regarded as a very essential part of the course in chemistry, and the teaching is so directed as to lead every student to recognise its importance. Constant reference is made to sources of information, to familiarise the student with the literature of chemistry, and that he may acquire a clear idea of the way in which different subjects have been built up. The object in view is, in fact, not only to make skilful workers, but clear thinkers.

I will conclude this reference to the arrangements for the teaching of chemistry in the United States, by a brief notice of two of the most important Technical Schools:—

Massachusetts Institute of Technology, at Boston.—Students from the Boston University receive their education in chemistry here. The following list of the teaching staff will give some idea of the comprehensive character of the scheme of instruction. The Professor of Metallurgy and Industrial Chemistry, J. M. Ordway; Professor of Organic Chemistry, J. M. Crafts; Professor of General Chemistry, W. R. Nicholls; Professor of Analytical Chemistry, C. H. Wing; Instructor in Chemistry and Mineralogy in the Women's Laboratory, Ellen H. Richards. There are besides several assistants. Assaying, and biology in its chemical aspects, are also taught.

On the occasion of my visit, I was fortunate enough to find Professor Ordway, who kindly showed me through the Institution. The first laboratory visited was that for women, where a number of

students were at work. The training of women in laboratory practice is indeed an important feature in this Institution. Courses of chemistry, open to both sexes, were commenced in 1867. A few years later the first course in quantitative analysis open to women was given. In 1876 new laboratories were opened; and in the first two years 43 women availed themselves of the instruction provided; about two-thirds of whom were either already teachers, or were preparing to teach.

The laboratories for qualitative and quantitative analysis were established in 1865, the laboratory for organic chemistry in 1877, and that for industrial chemistry in 1878–9. New laboratories were in course of construction at the time of my visit. At several institutions I found arrangements for the training of students in the working of ores on a somewhat practical scale; and I think it was here, as well as elsewhere, that I saw, for example, appliances for the working of half a ton of gold-bearing quartz, and in such cases the student was expected to get a good practical result.

Columbia College and School of Mines, New York City.—This School was opened in 1864; a new building, with extensive laboratories, was completed in 1874; and considerable extensions were in progress at the time of my visit. There are five regular courses of study: 1, mining engineering; 2, civil engineering; 3, metallurgy; 4, geology and palæontology; 5, analytical and applied chemistry. The Professor of Chemistry is Dr. C. F. Chandler, a Fellow of this Society, who kindly showed me over the Institution; and there are six or more instructors and assistants. General inorganic chemistry, stoichiometry, qualitative analysis, quantitative analysis, and blowpipe practice, are required in all the courses. Assaying is taught to the students in mining, metallurgy, and chemistry. In the geological and chemical courses, organic chemistry is studied.

For analytical chemistry there were three laboratories, one for qualitative, one for quantitative analysis, and a third for assaying; but as already intimated, the laboratory accommodation was undergoing very considerable enlargement.

In the third year, the subjects taken up by all the students in applied chemistry are:—1. Air (nature, sources of contamination, sewer gas, plumbing, drainage, disinfection, ventilation). 2. Water (composition of natural waters, pollution, disposal of sewage and house refuse). 3. Fuel, and its applications. 4. Artificial illumination (candles, oils and lamps, petroleum, gas and its products, electric light). 5. Lime, mortars, and cements. 6. Building stones (decay and preservation). 7. Timber and its preservation (pigments, paints, essential oils, varnishes). 8. Glass and ceramics. 9. Explosives (gunpowder, guncotton, nitro-glycerine, &c.).

In the fourth year the studies in analytical and applied chemistry are:—1. Chemical manufactures (acids, alkalis, and salts). 2. Food and drink (milk, cereals, starch, bread, meat, tea, coffee, sugar, fermentation, wine, beer, spirits, vinegar, preservation of food, tobacco, &c.). 3. Clothing (textile fabrics, bleaching, dyeing, calico printing, paper, tanning, glue, india-rubber, gutta-percha, &c.). 4. Fertilisers. 5. Organic chemistry (laboratory practice). 6. Assaying (ores of lead, silver, gold, platinum, tin, antimony, bismuth, copper, nickel, cobalt, iron, mercury, and zinc; also gold, silver, and lead bullion; mattes, slags, &c.). 7. Metallurgy (copper, lead, silver, gold, zinc, tin, mercury, &c.). 8. Economic geology (theory of mineral veins, ores, deposits and distribution of iron, copper, lead, gold, silver, mercury, and other metals; graphite, coal, lignite, peat, asphalt, petroleum, salt, clay, limestone, cements, building and ornamental stones, &c.). 9. Dissertation.

It will be seen that the course of study in this Institution is almost exclusively technical, being designed to train analysts and technologists rather than purely scientific investigators. A considerable amount of original research has, however, been conducted by the graduates, the results of some of which have been published.

With reference to the foregoing account of the arrangements for the teaching of chemistry, and for chemical research on the American Continent, whilst by some it may be thought to be inappropriately long for embodiment in the address of the President of the Chemical Society, it must, on the other hand, be looked upon as entirely inadequate to convey an idea of the extent of the provision for such teaching. My apology must be, on the one hand, that it was suggested to me that I should say something on the subject, and, on the other, that I have not had time, nor would it be suitable to appropriate space, for any more complete or detailed statement. Such as it is, I hope it will not be without interest, as giving some indication of the progress in the teaching of our science, and of the promise of original research, on the other side of the Atlantic. As already said, I must refer those who wish to know more to the official document which has been cited, whilst the manuscript supplement, which has, with great courtesy and much trouble, been drawn up for me, remains available for reference whenever further use can be made of it.

Since the last Anniversary Meeting, the Society has lost by death nine Fellows, and one Foreign Member. On the Home list, the losses are,—Mr. John Gray, Mr. Dugald Campbell, Mr. John Joseph Beaumont Jeanneret-Grosjean, Mr. Alexander Jesseman, Dr. George A. C. Pearce, Dr. G. W. Septimus Piesse, Mr. Edgar Wilcock, Professor

Henry John Stephen Smith, and Mr. Frank Hatton. On the Foreign list we have lost Frederic Wöhler.

Mr. John Gray, a native of Inverurie, Aberdeenshire, died suddenly on March 23, 1882, at the early age of 24. He had only a few weeks previously been elected Fellow of the Chemical Society. Mr. Gray received his chemical education at South Kensington, and in the laboratory of the Inland Revenue Department at Somerset House. He was a member of the analytical staff in that laboratory at the time of his death; and he was regarded by his superiors and his colleagues as a young man of great promise.

Mr. Dugald Campbell, Analytical and Consulting Chemist, of Quality Court, Chancery Lane, died at his residence, in Holland Road, Kensington, on May 12, 1882, at the age of 64. Mr. Campbell was a younger son of a good Scotch family, and was educated in Edinburgh. When quite a young man he went to Australia. On his return to this country, after a few years' absence, he devoted himself to the study of chemistry under the late Professor Graham, at University College, London; where he subsequently held the post of Demonstrator of Chemistry for a few years. Whilst in that position, he published (in 1869), his "Practical Text-book of Inorganic Chemistry," which had a considerable circulation at the time. Early in his career, he began to pay special attention to the subject of water analysis; and he assisted Dr. Clark, of Aberdeen, in his experiments on the process of water purification, with which his name is associated. He also paid much attention to the chemistry of sewage, and he was frequently consulted by sanitary authorities, and by the promoters of Waterworks. He was also frequently consulted by the Inland Revenue Department on questions of adulteration. Many years ago he conducted, in conjunction with Professor Graham and Dr. Stenhouse, an elaborate series of experiments with reference to the adulteration of coffee, the report of which was published in our Journal, to which he also contributed papers, "On the Application of Sewage to Agriculture," and "On the Source of the Water in the Deep Wells of the Chalk under London." To the *Philosophical Magazine* he contributed a short paper "On the Presence of Arsenic in River Sand," and in 1851 he communicated a paper to the British Association, "On the Effect of Magnesia on the Soap Test." Mr. Campbell held the appointment of chemist to the Brompton Hospital. He was entrusted by the Commissioners of Patents with the preparation of several volumes of their "Abridgments," among which may be mentioned those relating to "India-rubber and Gutta-percha," "Gas," "Medicine," "Oils, Fats, and Candles," "Acids, Alkalis, and

Salts," and "Sugar." He was also a frequent scientific witness in the Law Courts. Some years ago he was a Member of the Council of the Chemical Society, and more recently of the Council of the Institute of Chemistry. Mr. Campbell had been in a precarious state of health for some months, and the proximate cause of his death was an attack of paralysis.

Mr. John Joseph Beaumont Jeanneret-Grosjean, son of Pierre Frederic and Eliza Jeanneret-Grosjean, was born in Oxford Street, London, on May 3, 1843. He was educated at King's College School, where he took a prize for general proficiency. In 1862 he entered at Lincoln College, Oxford, being intended for the Church. Theological difficulties arising, he left Oxford after keeping one term; and in 1863 he entered the Regent's Park Baptist College. Whilst there he matriculated at the London University, taking honours in mathematics.

Mr. Grosjean finally gave up the idea of becoming a minister, and in 1864 entered as a student at the Royal College of Chemistry, under Dr. Hofmann. In 1866 he became assistant in the water-analysis laboratory under Dr. Frankland, and was soon distinguished by the care he took to render his work accurate. In August, 1867, Mr. Grosjean was appointed assistant to the Professor of Chemistry at the Royal Agricultural College, Cirencester. Here he remained two years. His patient assiduity in work, and his love of accuracy, were conspicuous, both in his teaching of the students and in his analytical and research work for Professor Church. During his stay at Cirencester he was engaged in investigations connected with turacin, namaqualite, cyclopic acid from Boer tea, oskelite, cornwallite, and ancient bronzes.

In the summer of 1869 Mr. Grosjean was engaged by Mr. (now Sir) J. B. Lawes, to proceed to Sicily to establish the manufacture of citrate of calcium at Palermo. Concentrated lemon juice had hitherto been the chief material employed by citric acid manufacturers in England. Mr. Lawes thought that, instead of concentrating the juice in Sicily, it might prove more economical to precipitate the raw juice with chalk, and to dry and export the resulting citrate. The production of citrate in Sicily had previously been attempted, but without success. Mr. Grosjean, however, succeeded in overcoming all difficulties, and since his visit considerable quantities of excellent citrate have been exported from Palermo.

On his return to England, in the spring of 1870, Mr. Grosjean was appointed assistant chemist at Mr. Lawes's tartaric and citric acid factory at Millwall; and in 1873 he became the principal chemist there. Mr. Grosjean remained at Millwall till his death. He

there devoted himself heartily to the improvement of analytical methods, and to the study of manufacturing operations. One paper, "On the Determination of Tartaric Acid in Lees and Inferior Argol, with some Remarks on Filtration and Precipitation," was communicated to the Society during his lifetime (Trans., 1879, 341). A selection from his unpublished investigations has since been brought before the Society, and will be found in the Journal for the present year. Mr. Grosjean was, during four years, 1872—1876, an Abstractor for the Society's Journal. He was one of the original Fellows of the Institute of Chemistry. He was also an active member of the Society of Chemical Industry, and served on the Committee of the London Section. Through life he was afflicted with partial deafness, and frequently suffered from ill health. He died on June 11, 1882, of congestion of the brain. He leaves a widow and three children.

Mr. Alexander Jesseman was for some years a schoolmaster under the London School Board. He had always shown a great predilection for science, and especially for experimental chemistry, to which he devoted most of his leisure time. Leaving the service of the London School Board, he attended several of the courses at South Kensington, and Jermyn Street; after which he was appointed Science Lecturer at Dulwich College. Here his health, always delicate, gave way under the pressure of the duties which devolved upon him. He did not cease work until compelled to take to his bed, and he died on July 19th, 1882. Mr. Jesseman was elected a Fellow of this Society in December, 1880.

George A. C. Pearce, M.B., late of Dane's Inn, London, and Lee, Kent, died at Cadiz on October 5th, 1882, at the early age of 31, and was buried in the British Cemetery there. Dr. Pearce was educated at Bristol, and afterwards at Trinity College, Dublin; where he obtained the Medical Scholarship in 1871, and the Moderatorship in Experimental Science in 1872, the attainment of the latter honour being chiefly the result of his answers in chemistry. He further obtained the degree of Bachelor of Medicine in the University of Dublin in 1873, and the degree of Master in Surgery in 1874, coming first in the examination. In the summer of 1872 he became assistant, under Professor Apjohn, in the Laboratory for Medical Students, and Dr. Apjohn states that he gave both himself and the class the fullest satisfaction. Dr. Pearce was elected a Fellow of this Society in 1877. Of late years he was engaged in commercial pursuits, but he always retained a love for science, and was intending to resume medical practice, when disease of the lungs, which caused his death, became developed.

George William Septimus Piesse, Ph.D., was the son of the late Mr. Charles A. J. Piesse, chief clerk in the War Office. He was born on May 30th, 1820, and died on October 23rd, 1882. His early education was at a grammar school. He always exhibited a taste for science, and first gave serious attention to optics; and although he had served no apprenticeship to the business, he started life as a practical optician. Want of capital, however, prevented his continuing in this occupation. He next studied chemistry, attending the lectures of Professor Graham, at University College, London. For some time he practised as an analytical chemist; but giving this up, he again turned his attention to business, and became engaged, first with Messrs. J. and C. Atkinson, the perfumers, afterwards with the late Mr. Breidenbach, and finally joined with Mr. Lubin in founding the firm of Piesse and Lubin. This firm cultivated perfume-bearing plants in the South of France; and Dr. Piesse for many years endeavoured to promote the cultivation of such plants in the British Colonies, and succeeded in inaugurating numerous experiments in this direction, some of which are still in progress. Dr. Piesse early became an Associate of the Chemical Society, and was elected a Fellow in December, 1862. He contributed a paper, "Observations on Brewing," and another, "Certain Impurities in Commercial Sulphate of Copper." He was also the author of "The Art of Perfumery," "Piesse's Magic," "Laboratory of Chemical Wonders," "Twenty Letters on Farming," &c. He contributed the articles on Perfumery, and kindred subjects, to several Cyclopædias; and for a period of about 25 years he wrote the "Scientific and Useful" column in the *Family Herald*.

Mr. Edgar Wilcock received his early education at the City of London School; and he afterwards studied at the Royal College of Chemistry, South Kensington, for nearly four years. Although frequently in delicate health, he studied very diligently, and passed through the usual course of instruction, and the examinations of the College, with much success. In the Research Laboratory there, Mr. Wilcock conducted investigations, in conjunction with Dr. Japp, the results of which were published in their joint names, in the Society's Journal as follows:—"On the Action of Benzaldehyde on Phenanthraquinone, both alone and in presence of Ammonia" (1880 [i], 661); and "On the Action of Aldehydes on Phenanthraquinone in presence of Ammonia" (second notice, 1881 [i], 225). Mr. Wilcock was elected a Fellow of the Chemical Society in February, 1880; and at the time of his death, which took place on January 21st, 1883, he was Senior Assistant to Dr. Tidy.

Professor Henry John Stephen Smith, M.A., D.C.L., F.R.S., died

at Oxford on February 9th, 1883, in his 56th year. He was an Irishman by birth, but passed almost the whole of his life in England. His father was a member of the Bar, but died whilst his son was still quite young. Henry Smith was educated at Rugby, and afterwards at Oxford. He had left school in ill health, and was ordered to abstain from study for a year or more before he went into residence at Oxford. He was elected a scholar of Balliol in 1846, and in 1848 carried off the Ireland Scholarship. In the following year he obtained a Double First Class in Classics and Mathematics, and in 1851 he was elected to the Senior Mathematical Scholarship. He succeeded in due course to a Fellowship at Balliol, which he held till a few years ago, when he was elected to a Professor Fellowship at Corpus. In 1861, after the death of the late Professor Baden Powell, he was appointed his successor as Professor of Geometry.

Some years previously Mr. Smith devoted some time to the study of Chemistry, working in the Laboratory of the Ashmolean Museum, under Professor Maskelyne, who says that he went to work just like an old hand, having read the methods of separation, and made himself so well acquainted with them. He, however, took more interest in the general principles of chemistry than in its details. He became a Fellow of the Chemical Society in January 1854. By his death we have lost a very distinguished Fellow, though it was not in the domain of chemistry that his distinction was won. In the scientific world, not of England alone, he attained his greatest eminence as a mathematician. He was, however, a man of the widest acquirements, and of the widest sympathies with all branches of knowledge. He was a brilliant conversationalist, a good linguist, and in the best sense a consummate man of the world. He was associated with almost all the movements, scientific, political, and philanthropic, in Oxford, and was also much occupied with work of various kinds in London. For years he was a member of the Hebdomadal Council, and took an active share in all the legislative work of the University. In 1874 he succeeded the late Professor Phillips as Keeper of the University Museum, at Oxford. It was in this capacity that he became officially associated with the Professors of the various branches of science taught in that Institution. In the exercise of his duties he showed the greatest tact, judgment, and courtesy; and it was here that his influence in the furtherance of scientific education in the University was the most felt. He was a member of the late Royal Commission on Scientific Education; and it is believed that a considerable portion of its very able Report was drafted by his pen. He was also a member of the University of Oxford Commission, under Lord Salisbury's Act. Among his numerous engagements in London, he was Chairman of the Meteorological Council, which may be looked

upon, so to speak, as the Weather Department of the United Kingdom. He has served on the Council of the Royal Society, and also on the Council of the British Association. In fact, he possessed unusual capacity for practical business, and from his charm of manner, and tact, he exercised a unique personal influence, both in Oxford and elsewhere.

Professor Smith was the author of many mathematical papers of a high order, which are highly esteemed by mathematicians on the Continent, as well as in this country. Indeed, even since his death it has been announced that the Academy of Sciences (Paris) has awarded *ex equo*, to him and to M. Minskowsky, the "Grand Mathematical Prize."* Owing to his very full occupation in other ways, Professor Smith has given but little permanent literary work to the world. Among others, mention may be made, however, of an essay on the "Plurality of Worlds," reviewing the controversy between Whewell and Brewster, which was published in the first volume of the "Oxford Essays." Although Professor Smith was only in a limited sense a chemist, we may be proud that his name was on our list of Fellows, and we must deeply regret his premature death.

Mr. Frank Hatton was the only son of Mr. Joseph Hatton, Author and Journalist. The newspapers of Monday last (March 26th) record his death, in Borneo, whilst out elephant hunting, when his rifle caught in the bushes, and he was thus accidentally shot through the lungs, and died instantly. A career of something more than promise was thus closed at the early age of 22. Mr. Frank Hatton was educated at the College of Marcq, Lille; King's College School, London; the School of Mines, Jermyn Street; and the College of Chemistry, South Kensington. Dr. Frankland writes that he was one of the most genial, earnest, and talented students he has had in his laboratory; a most indefatigable worker, and a skilful manipulator. Dr. Frankland adds that Mr. Hatton's investigations on the influence of various gases on Bacteria constitute, in his opinion, a very valuable contribution to our knowledge of the principles of disinfection and of the arrest of zymotic disease. In a recent discussion at the Institution of Civil Engineers, Dr. Frankland referred to the researches in question as having proved that the only practicable material capable of destroying bacterial life in drinking water was spongy iron—a substance which had been applied on a large scale with marked success at the Antwerp Waterworks. Mr. Hatton was elected a Fellow of the Chemical

* Since the above was in type, it has been announced that the Academy, having found that Minskowsky had simply pirated Professor Smith's communication to the Royal Society in 1868, has declared the whole prize to have been gained by Professor Smith.

Society in December, 1879; and he has contributed three papers to our Journal—1. "On the Action of Bacteria on Gases" ([i], 1881, 247—258). 2. "On the Oxidation of Organic Matter in Water by Filtration through various Media; and on the Reduction of Nitrates by Sewage, Spongy Iron, and other Agents" ([i], 1881, 258—276). 3. In conjunction with Dr. Hodgkinson, "On the Reduction of Cinnylic Alcohol" ([i], 1881, 319—320). His research on the influence of gases on Bacteria won for him the Frankland Prize, as well as the Associateship of the Institute of Chemistry. In 1881 Mr. Hatton was appointed scientific explorer to the British North Borneo Company. He had successfully borne the hardships of travel in North Borneo, exploring the greater part of the Company's territory. For his work in Borneo he had qualified himself by unremitting labour. He spoke and wrote the languages of the country—Malay and Dusun; and at the time of his death he was engaged in preparing a Dictionary of the latter language. The reports he had already sent home covered a wide range of scientific exploration—geographical, geological, and otherwise; extracts from which have already been published by the Company for private circulation. In his last letter he announced that he was going on an expedition down the Seguama river to Mount Salam, whence he was to return to Elopuran, and thence to England. The fact that he died near Elopuran indicates that he had successfully accomplished this, his latest official mission. It is understood that he was keeping a diary for publication on his return home. Mr. Hatton's body is to be brought to England for interment; and his diaries will be collected and published. I will conclude this notice with a quotation from a letter which I have received from Dr. Frankland, dated March 28:—"Mr. Frank Hatton was a young chemist of very great promise, who would certainly, had he lived, have communicated to the scientific world important observations resulting from his explorations in Borneo. The untimely death of such an accurate, acute, and trained observer is a serious loss to science."

Friederich Wöhler was born on the 31st of July, 1800, at Eschersheim, near Frankfort, and he died at Göttingen, on September 23, 1882.

Neither space nor time will permit anything like an exhaustive review of the lifework of Wöhler to be given on this occasion. Only a short account of the principal facts of it can be given. This is extracted from a Work by Professor Hofmann ("Zur Erinnerung an Wöhler"), the advance proof-sheets of which he has kindly forwarded for the purpose to our Foreign Secretary, Dr. Hugo Müller, to whom I am indebted for the following abstract in English:—

In Wöhler, we have lost one of the veterans of our science. Born almost at the commencement of modern chemistry, he was himself one of the principal founders of organic chemistry; and by his unceasing and brilliant contributions during a long and active life he helped largely to raise the edifice of chemistry generally.

Wöhler's father, who was a man of very general accomplishments, had held for some time the post of Equerry to Prince Wilhelm II of Hesse, and afterwards a similar post in the service of the Duke of Meiningen, where, more especially by his various improvements in the agriculture of the little Principality, he attained a very influential position. Later, he became the proprietor of an estate at Roedelsheim, near Frankfort, and six years afterwards he was induced by the Prince-Primus Dahlberg to accept the post of Equerry at the Grand Ducal Court, and to reside at Frankfort. In this new position Wöhler's father became one of the most honoured citizens of Frankfort, and his memory still lives in connection with a variety of educational institutions and societies.

It was thus under the most favourable conditions that Wöhler began his educational career, entering, in 1814, the High School (Gymnasium) at Frankfort. In his predilection for the study of nature he received every encouragement from his father and others; and even at that time he took great delight in collecting minerals and in performing chemical experiments. Amongst the latter, we may mention the preparation of potassium by Curandau's process, which sufficiently indicates the degree of skill in chemical operations that he must have already attained.

The first paper by Wöhler, "On the occurrence of Selenium in the Iron Pyrites of Kraslitz, in Bohemia," was published at this time.

The time had now arrived for him to make up his mind as to what profession he should choose, and he decided for Medicine. He went, in 1820, to the University of Marburg, where he attended lectures on physics, mathematics, and anatomy. But as this University did not, at that time, afford a favourable opportunity for practical work in chemistry, he improvised a laboratory in his private rooms, and there pursued an investigation on certain cyanogen compounds.

He stayed, however, only one year at Marburg, and then exchanged this University for that of Heidelberg, to which place he was especially attracted by the enthusiasm he felt for Leopold Gmelin, who now became his teacher, and soon his friend and counsellor. Whilst at Heidelberg, he gave himself up to the study of medicine, but at the same time he carried on his researches on cyanic acid, the results of which he published in two papers, in 1822 and 1823. In this work we recognise the prelude to the famous investigation which later led to the artificial production of urea.

It was at this time that Gmelin and Tiedemann were engaged upon their chemico-physiological investigations. Tiedemann took a great personal interest in Wöhler, and to this is probably due the interest Wöhler took hereafter in the study of physiology. At this time he gained the prize for an essay on "Excretion in the Urine of Substances Foreign to the Animal Organism, but which are introduced into the Body." He proved the transformation of the salts of some of the fruit-acids into carbonates; whilst oxalic acid, succinic acid, and gallic acid, reappear in the form of alkaline salts.

Wöhler had as yet no idea of giving up the profession of medicine, to which he was ardently devoted; and it was only in the autumn of 1823, when he had already passed his examinations with distinction, that Gmelin persuaded him to give to his career a different direction, and to devote himself for the future entirely to chemistry. As he felt assured of his father's acquiescence, he was not long in deciding.

Soon afterwards, Wöhler was fortunate enough to receive permission from Berzelius to go to Stockholm, and work in his laboratory. Wöhler in his "Jugend-erinnerungen eines Chemikers," *Berlin Berichte*, 1875, has given a charming account of his sojourn in Sweden, and of the lasting friendship with Berzelius to which it led. Whilst in Berzelius's laboratory he occupied himself principally with mineral chemistry and quantitative analysis, in order to make himself thoroughly acquainted with the methods and manipulation of the great master. Later, he continued his researches on cyanic acid.

Towards the end of 1824 he returned from Sweden; and on paying a visit to his friends at Heidelberg, it was decided that he should attach himself to the University there, as "privat-docent" in chemistry. In order to prepare himself for the necessary formalities to be gone through for this purpose, he returned for a while to his father's house at Frankfort. But before his plans with regard to Heidelberg were realised, he was induced to change them in favour of taking the teachership of chemistry at the newly-founded municipal Trade School (Gewerbeschule) at Berlin, and on March 25th he commenced his new career there.

Having now, for the first time, a laboratory of his own, he began to work with more than his usual energy, though his time was well taken up by his official duties, and with the translation of Berzelius's work.

One of the earliest results of his new activity at Berlin was the preparation of the metal aluminium, soon followed by that of beryllium and yttrium. A great number of papers, chiefly on metallic compounds and minerals, date from this time. But all these investigations were put into the shade, when, in 1828, as an outcome of his long-continued research on cyanogen compounds, he dis-

covered the artificial production of urea. As the first example of the synthesis of a body hitherto only known as a product of animal life, this discovery will for ever hold its place as one of the most prominent landmarks in the development of organic chemistry.

In speaking of the lifework of Wöhler, it is impossible to omit reference to the many investigations of the highest importance which he carried out conjointly with Liebig.

It was shortly after Wöhler had returned from Sweden that he and Liebig met for the first time at Frankfort. They at once conceived a great interest for each other, which, in the course of time, developed into the most intimate and enduring friendship. Liebig was already Professor at Giessen, and Wöhler, going shortly afterwards to Berlin, their intercourse was mainly kept up by correspondence; although, in later life, they met in vacation times, and sometimes travelled together.

From the letters which form the earlier part of this correspondence, we obtain an interesting history of the important investigations which were conceived and carried out by them conjointly: such as on cyanic acid, 1830; on oil of bitter almonds, 1832; on the formation of the oil of bitter almonds, 1837; on uric acid, 1838; and others. On reading the accounts of these investigations by the light of these letters, we cannot help being struck by the happy coincidence which united two such powers for the pursuance of one common object.

Towards the end of 1831 Wöhler gave up his position at Berlin, and shortly afterward accepted a similar one at the newly established "Gewerbeschule" at Cassel. This he held until 1836, when he was appointed successor to Stromeyer in the Professorship of Chemistry at Göttingen.

It was whilst at Cassel that the famous work on "Oil of Bitter Almonds, or Compounds of Benzoyl," was carried out, conjointly with Liebig; an investigation which must undoubtedly be considered one of the most beautiful and fruitful of their associated labours. Even at the present day, we are struck by the completeness of experimental evidence, and the concise reasoning displayed, in this investigation. How vast and far-reaching has been the influence of this inquiry in giving direction to our conceptions of the general nature of chemical compounds. The admiration which this work calls forth even now, after the lapse of many years, was, however, equally felt, and expressed with enthusiasm, by contemporaries. Berzelius gave it as his opinion, that the facts put forward by this research give rise to such considerations, that they may well be deemed the beginning of a new era in vegetable chemistry.

Some years afterwards (in 1837), Liebig and Wöhler returned once more to the same subject, but this time with the view of inquiring into

the origin of this essential oil, which at that time was still shrouded in mystery. It is well known in how masterly a manner this problem was solved, and how the formation of this body was traced to the remarkable metamorphosis which amygdalin undergoes when submitted to the ferment-like action of emulsin. This action of the decomposition of amygdalin subsequently became a typical one.

Limited as our space here is, we must not omit to allude, if only a few words, to another of those joint works of Liebig and Wöhler, viz., the investigation on "Uric Acid and its Derivatives." The little that was known about uric acid at the time when the subject was taken up by the two investigators was far from definite, and these researches present a picture of the most indefatigable struggle to obtain an insight into the apparently unlimited mutability which characterises this substance. But this liability to chemical change, produced, on the other hand, such a harvest of results as has seldom fallen to the lot of chemical investigators. The numerous and remarkable substances which were brought to light by this research afford striking evidence of the skill in manipulation, and of the scrupulous accuracy, with which the experiments were conducted.

We must content ourselves here with this scanty notice of some of the joint work with which Liebig and Wöhler have endowed our science, and return to Wöhler's own labours.

It would lead too far, were we to attempt to give an account even of the more prominent of the vast number of papers published by Wöhler during his long and active life. In the Royal Society Catalogue of Scientific Papers there are about 270 papers and notices recorded under his name, ranging over all branches of chemistry, thus manifesting his marvellous versatility; and there are besides between 40 and 50 papers of which he was joint author.

But admirable and meritorious as this useful activity may have been, there is still another aspect in which we have to view the services rendered by Wöhler to science. It is his function as a teacher to which we allude. From the time when he entered on his professorship in 1836, up to within a few years before his death, he attracted to Göttingen a never ceasing stream of pupils, who came from all parts of the world to pursue the study of chemistry under his guidance.

His kindly disposition, and the geniality of his manners, endeared him to his students. His never failing originality in devising new methods, and his skill in manipulation, were eminently calculated to inspire the youthful mind with ardour for work, and to kindle enthusiasm for the pursuance of science. Many of the active chemists of the present generation, both in Europe and America, have enjoyed the advantages of Wöhler's instruction, and owe their success in their

career to the impulse given to their studies whilst in the laboratory at Göttingen.

Dr. Schunck said that all must regret that Dr. Gilbert was not in a position to accept the office to which he had been nominated by the Council. The Fellows were much indebted to him for his constant attendance and courtesy. He had much pleasure in proposing a hearty vote of thanks to Dr. Gilbert, and that his Report be adopted.

This was seconded by Prof. Ronalds, and carried unanimously.

Dr. Gilbert said he appreciated very highly the honour of having been President of the Chemical Society, and most sincerely regretted that, in consequence of the pressure of his own avocations, and the distance he lived from London, he had been obliged to relinquish the position at the end of the first year. His successor, Dr. Perkin, was a tried officer of the Society, and had by his communications contributed largely to the interest both of the Meetings, and of the Journal; and it seemed only fitting that a chemist who had devoted himself specially to organic chemistry should fill the office of President, when so many contributions relating to that branch of the science were brought before the meetings of the Society.

The Treasurer then presented his Report. The total income of the Society was about £3073, the expenditure about £2770, leaving a surplus of £303. The surplus was rather smaller than last year for several reasons. There had been an increase in the expense connected with the Journal of £217; with the library of £61; the income was also rather less than was anticipated, owing to the fact that a smaller proportion than usual of the new Fellows had compounded. Next year there would probably be no surplus, as it would be taken up by the expenses connected with the new catalogue, and the re-decoration of the Society's rooms. The assets of the Society consisted of £7788 stock, and a balance at the bank of £1194. As to the Research Fund, £220 had been given in grants during the year. The assets consist of £4500 stock, and a balance at the bank of £166. The donations to the fund had fallen off considerably.

Mr. Warington proposed a vote of thanks to the Treasurer, which was seconded by Mr. Makins, and carried unanimously.

Votes of thanks were given to the Auditors, the Council and Officers, and the Editor, Sub-editor, and Abstractors.

Messrs. W. Thorp and J. A. R. Newlands were then nominated Scrutators, and the following Officers and Council were declared duly elected:—

President.—W. H. Perkin, Ph.D., F.R.S.

Vice-Presidents.—F. A. Abel, Warren de La Rue, E. Frankland, J. H. Gilbert, J. H. Gladstone, A. W. Hofmann, W. Odling, Lyon

Playfair, H. E. Roscoe, A. W. Williamson, A. Crum-Brown, P. Griess, G. D. Liveing, J. E. Reynolds, E. Schunck, A. Voelcker.

Secretaries.—H. E. Armstrong, J. Millar Thomson.

Foreign Secretary.—Hugo Müller.

Treasurer.—W. J. Russell.

Council.—E. Atkinson, Capt. Abney, H. T. Brown, W. R. E. Hodgkinson, D. Howard, F. R. Japp, H. McLeod, G. H. Makins, R. Meldola, E. J. Mills, C. O'Sullivan, C. Schorlemmer.

RESEARCH FUND.

During the past year grants from the Research Fund have been made as follows, on the recommendation of the Research Fund Committee:—

£100 to Dr. Wright for the continuation of his research on the Determination of Chemical Affinity in Terms of Electromotive Force.

£25 to Messrs. Cross and Bevan for the investigation of Certain Varieties of Cellulose.

£25 to Dr. Rennie for the further investigation of Australian Sarsaparilla.

£25 to Mr. Shenstone for the further investigation of the Nux Vomica Alkaloïds.

£15 to Mr. Watson Smith for the investigation of a Sublimate formed in the Manufacture of Aurin.

£25 to Professor Tilden for the investigation of the C_5H_8 Hydrocarbons and the Decomposition of Terpenes by Heat.

£10 to Mr. James for the investigation of Ethylene Chlorobromide and its Homologues.

Dr. The Treasurer in Account with the Chemical Society from March 24, 1882, to March 21, 1883. Cr.

	£	s.	d.	£	s.	d.
Balance at Bank March 24th, 1882	1,420	8	10			
,, in hands of Treasurer	1	16	7			
				1,422	5	5
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 24th, 1882, to March 21st, 1883.						
10 Life Compositions	200	0	0			
114 Admission Fees	456	0	0			
11 Subscriptions for 1880	22	0	0			
53 ,, ,, 1881	106	0	0			
240 ,, ,, 1882	464	0	0			
615 ,, ,, 1883	1,194	3	6			
1 ,, ,, 1884	2	0	0			
				2,444	3	6
Sale of Journal and Index				328	16	6
Subscriptions for Proceedings of Royal Society				37	10	0
,, from Institute of Chemistry	8	10	0			
,, ,, Public Analysts	4	0	0			
,, ,, Society of Chemical Industry	4	15	0			
				17	5	0
Dividends on Consols	116	15	0			
,, Metropolitan Board of Works Stock	98	0	10			
,, London and North Western Railway Debenture Stock	30	14	3			
				245	10	1
				4,495	10	6

Assets.	£	s.	d.
Balance at Bank	1,194	10	9
,, in Treasurer's hands	1	11	8
Three per Cent. Consols	4,000	0	0
London and North Western Railway Debenture Stock	788	0	0
Metropolitan Board of Works 3½ per cent. Stock	3,000	0	0

Expenses on Account of Journal.	£	s.	d.	£	s	d.
Salary of the Editor	250	0	0			
,, Sub-Editor	100	0	0			
Fees to Abstractors	312	2	11			
Incidental expenses of Editor	3	0	0			
Periodicals for use of Abstractors	39	9	0			
Distribution of Journal	187	0	6			
Printing of Journal	1,011	0	10			
Photographic Printing of Spectra	42	0	0			
				1,944	13	3
Expenses on Account of Library.						
Salary of Librarian	50	0	0			
,, Library Attendant	62	0	0			
Books and Periodicals	149	10	8			
Binding Books	45	19	2			
				307	9	10
Printing Authors' Copies				25	7	0
Proceedings of Royal Society, and Distributing same				36	0	0
Reports of Meetings				24	0	0
Miscellaneous Printing				31	7	0
Insurance of Furniture and Books				2	0	0
Inhabited House Duty and Income-tax				8	13	1
Stationery, Postage, &c.				37	7	6
Collector's Commission on Subscriptions				122	3	0
Treasurer's Stamps and Clerical Aid and Drafts				5	2	3
Expenses connected with Prof. Dewar's Lecture				4	10	0
Photographs of Presidents				6	6	0
House Expenses.						
Providing Refreshments at Meetings	21	9	10			
Heating the Building	20	2	0			
Lighting ,,	52	19	10			
Cleaning ,,	20	0	0			
Wages of House Porter	52	0	0			
Petty House Expenses	11	9	6			
Repairs and Alterations	20	18	10			
Three Ballot Boxes	12	12	0			
Gratuity to Gate Porters	2	2	0			
				213	14	0
Treasurer's Petty Cash Disbursements				0	15	2
April 26th. Purchase of £500 Metropolitan Board of Works 3½ per cent. Stock				530	0	0
Balance in Bank	1,194	10	9			
,, in hands of Treasurer	1	11	8			
				1,196	2	5
				4,495	10	6

Examined and found correct. { Leonard Temple Thorne, W. R. Eaton Hodgkinson, David Howard.

THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.
FROM MARCH 24TH, 1882, TO MARCH 21ST, 1883.

DR.

	£	s.	d.
Balance at Bank, March 24th, 1882	341	2	10
Subscriptions and donations	120	1	0
Dividend on North British Railway Stock	19	10	2
,, Metropolitan 3½ per cent. Stock	117	13	3
	£598	7	3

CR.

	£	s.	d.
July, 1882. Grants made	125	0	0
Jan., 1883. Grants made	95	0	0
Purchase of £200 Metropolitan 3½ per cent. Stock	212	0	0
Balance	166	7	3
	£598	7	3

Assets.	£	s.	d.
North British Railway 4 per cent. Stock	1,000	0	0
Metropolitan Board of Works 3½ per cent. Stock	3,500	0	0
Balance at Bank	166	7	3

Examined and found correct,

LEONARD TEMPLE THORNE,
W. R. EATON HODGKINSON,
DAVID HOWARD.

XXXII.—*On the Estimation of Hydrogen Sulphide and Carbonic Anhydride in Coal-gas.*

By Lewis T. Wright.

The estimation of hydrogen sulphide and carbonic anhydride in coal-gas is not without difficulties, for unpurified coal-gas is a complex mixture—a mixture whose components are far from being all known. In cases where the method of estimating the hydrogen sulphide and carbonic anhydride is absorptiometric, as in Bunsen's and other gas-analysis methods which depend on the principle of the measurements of absorbed volume, it is customary to term that portion of the gas absorbed by such reagents as manganic peroxide, ferric oxide, &c., hydrogen sulphide; and that portion of the gas which may be absorbable by potassium hydroxide and not by manganic peroxide, &c., is considered as carbonic anhydride. It must be admitted that the portion of the gas under analysis termed hydrogen sulphide (an amount perhaps closely and practically approximating to the true amount) is really hydrogen sulphide, plus other gases of more or less unknown composition; and further that the portion termed carbonic anhydride is really carbonic anhydride, plus other bodies.

With this reservation there can be no particular objection to such a method of stating analysis. But however valuable may be the absorptiometric methods for the estimation of hydrogen sulphide and carbonic anhydride in coal-gas, when the sample of gas has to be transported from its place of collection to the place of analysis, or where the supply may be small and large quantities not available, I think it possible that there are other methods more generally applicable, especially where the hydrogen sulphide and carbonic anhydride exist only as a very small percentage. In practice the united amount of these two impurities in unpurified coal-gas ranges from about 2 to 4 per cent., and in partially purified or finished coal-gas will range from that amount to nullity.

Being anxious to determine the degree of accuracy to which hydrogen sulphide and carbonic anhydride could be estimated in coal-gas by absorptiometric gas-analysis, I made some experiments with an apparatus of the Frankland-Ward type, which are instructive and interesting with regard to the use of solid porous reagents.

Bunsen (*Gasometrische Methoden*, 1877) publishes some analyses from which, of course, it is not possible to draw safe conclusions in reference to the estimation of hydrogen sulphide in coal-gas, for the mixtures he analysed were simple and artificially prepared.

Operating with a manganic peroxide bullet moistened with syrupy phosphoric acid, according to the method fully described in his work, he obtained the following results:—

Analysis 18.

	Employed.	Found.
CO_2	46·60	46·59
H	20·51	20·50
H_2S	32·89	32·91
	100·00	100·00

Analysis 19.

	Employed.	Found.
CO_2	82·16	82·49
H_2S	17·84	17·51
	100·00	100·00

The numbers in analysis 18 are very good indeed, but the difference in analysis 19, viz., 0·33 per cent. on the total volume of the mixture analysed, is serious.

The system adopted in my experiments can be briefly described. Test-tubes containing about 60 c.c. were filled over mercury with crude coal-gas (free from ammonia-vapours), and were kept sealed with mercury in small porcelain crucibles.

It is true that mercury is attacked by hydrogen sulphide, but the error due to this is infinitesimal when the gas is in contact with mercury for a few hours. In 20 to 48 hours I have noticed a slight loss of hydrogen sulphide from this cause. In the following experiments the gas was analysed as soon as collected:—

One-half of the sample of coal-gas was passed into the laboratory tube which, together with the measuring tube, had been freshly washed out. It was then passed into the measuring tube, measured, and transferred to the laboratory tube; then treated with some solid reagent for hydrogen sulphide absorption for half an hour; then remeasured; again brought back into the laboratory tube, treated with a few drops of potassium hydroxide solution, and again measured.

The hydrogen sulphide and carbonic anhydride were thus separately determined. The laboratory and measuring tubes were again washed to bring them into the same condition as at the commencement of the first analysis. The remaining portion of the gas sample in the test-tube was then passed into the laboratory tube, measured, and treated

with a few drops of potassium hydroxide solution previously saturated with clean coal-gas, and the resulting absorption determined.

The hydrogen sulphide and carbonic anhydride were thus determined together.

First Series.

The reagent for hydrogen sulphide absorption was a manganic peroxide bullet prepared, introduced, and removed from the laboratory tube in the manner indicated by Bunsen. The same bullet served for the three absorptions, but was treated with syrupy phosphoric acid between each absorption.

	H_2S with MnO_2.	CO_2 with KHO.	Total.	$CO_2 + H_2S$ with KHO.	Difference.
1	0·971 p. c.	1·024 p. c.	1·995 p. c.	2·319 p. c.	0·324 p. c.
2	0·955 „	1·420 „	2·375 „	2·679 „	0·304 „
3	0·955 „	1·066 „	2·021 „	2·185 „	0·164 „

The conclusions I arrive at from this series is that the manganic peroxide bullet introduced a small quantity of gas; the amount so introduced decreasing each time the bullet was used.

Second Series.

The same manganic peroxide bullet used as in first series, but it had been placed in a tube and submitted to the action of a current of clean coal-gas for some hours.

	H_2S with MnO_2.	CO_2 with KHO.	Total.	$CO_2 + H_2S$ with KHO.	Difference.
1	0·956 p. c.	1·083 p. c.	2·039 p. c.	2·019 p. c.	0·020 p. c.
2	1·046 „	1·189 „	2·235 „	2·219 „	0·016 „
3	1·010 „	1·217 „	2·227 „	2·210 „	0·017 „

A great improvement is here manifested, due no doubt to the "saturation" of the manganic peroxide bullet; but it will be noticed that the error is reversed: a small quantity of gas being removed mechanically with the bullet.

Third Series.

With pellets of cupric sulphate dried at 150°.

	H_2S with $CuSO_4$.	CO_2 with KHO.	Total.	$CO_2 + H_2S$ with KHO.	Difference.
1	1·120 p. c.	1·060 p. c.	2·280 p. c.	2·130 p. c.	0·150 p. c.
2	0·976 „	1·016 „	1·992 „	1·598 „	0·394 „
3	0·902 „	1·002 „	1·904 „	1·491 „	0·413 „
4	0·641 „	1·520 „	2·161 „	1·780 „	0·381 „

The porous cupric sulphate had absorbed mechanically some gas; but the error, though in the reverse direction, is not much greater than was the case in the first series with manganic peroxide.

Fourth Series.

With pellets of cupric phosphate moistened with syrupy phosphoric acid.

	H_2S with Cu. ph.	CO_2 with KHO.	Total.	$CO_2 + H_2S$ with KHO.	Difference.
1	1·323 p. c.	1·540 p. c.	2·863 p. c.	2·696 p. c.	0·167 p. c.
2	1·224 „	0·999 „	2·223 „	1·981 „	0·242 „
3	1·730 „	1·050 „	2·780 „	2·380 „	0·400 „

It will be seen from the second series that hydrogen sulphide and carbonic anhydride can be separately estimated with a considerable degree of nicety by means of a manganic peroxide bullet "saturated" with clean coal-gas, and potassium hydroxide similarly treated.

For many reasons I prefer, for the estimation of hydrogen sulphide and carbonic anhydride in impure coal-gas, a method founded upon the increase in weight of absorption-tubes: a method which will admit of the use of a tolerably large quantity of gas collected regularly during an interval of time sufficiently long to afford an idea of the average composition of the gas supply to be tested. I had long used a method founded upon one described by Fresenius (*Quantitative Analysis*, 1876, p. 341), in which the desiccated gas is first passed through tubes containing cupric sulphate on pumice dried at 150°, and then through tubes containing soda-lime for carbonic anhydride absorption.

Fresenius recommended a very elaborate train of apparatus, which would have to be still more elaborate in the case of crude coal-gas, on

account of the small absorbing power of cupric sulphate on pumice for hydrogen sulphide.

The modification I recommended was chiefly in the use of cupric sulphate without pumice, and a general simplification of the train to as few pieces as possible. A full description of this method as applied to coal-gas was published in the *Journal of Gas Lighting* (**39**, 422). I then pointed out as a source of error the formation of organic sulpho-acids due to a reaction between the hydrocarbon vapours present in coal-gas, and the hydric sulphate liberated by the reaction between cupric sulphate and hydrogen sulphide. However, there are other objections to the use of cupric sulphate as an absorbent for hydrogen sulphide, which would apply in cases where hydrocarbons are altogether absent. The first objection is the formation of sulphurous anhydride. Fresenius (*Quantitative Analysis*, 1876, p. 382), in describing the method of preparation of the cupric sulphate pumice, directs that it is to be dried for four hours at a temperature of 150—160°. "If the prepared pumice is dried at a lower temperature it takes up much less of the gas (H_2S); if dried at a higher temperature the gas is decomposed, and sulphurous acid is formed." I have prepared numerous samples of cupric sulphate at the temperature indicated by Fresenius, and have found that all, without exception, yield large quantities of sulphurous anhydride under the action of hydrogen sulphide, and I have also found this action to take place in cases where the cupric sulphate had been dried at temperatures lower than 150°. Again, cupric sulphate is not always very sensitive to very small quantities of hydrogen sulphide diluted with other gases.

I therefore sought for another reagent free from the inconveniences attending the use of cupric sulphate, and have tried amongst other substances, mercuric oxide, ferric oxide, and manganic peroxide.

The samples of hydrated ferric oxide I have tried are not very sensitive for the last traces of hydrogen sulphide; the same remark applies to manganic peroxide. I have made trials with mercuric oxide, but find that this body constantly loses weight in a current of coal-gas.

Coal-gas perfectly freed from hydrogen sulphide and carbonic anhydride was first passed through a drying cylinder containing calcium chloride, and then through a **U**-tube charged with mercuric oxide and calcium chloride, a piece of cotton wool separating the two reagents. The **U**-tube was weighed full of coal-gas at the commencement and termination of each experiment.

(1.)	0·45 cubic foot gas.	Tube lost	0·2	grain.
(2.)	0·85 „	„	0·9	„
(3.)	4·90 „	„	4·9	„

It would appear that mercuric oxide loses weight in clean coal-gas to the extent of 1 grain per cubic foot of gas. I have not made any attempt to discover the cause of this loss of weight, and am not able to explain the action.

When pure hydrogen sulphide is passed into a tube containing dry mercuric oxide, a violent action takes place, sulphurous anhydride being formed, and mercuric sulphide volatilised.

I have finally adopted as the reagent for absorption of hydrogen sulphide in absorption tubes, a cupric phosphate, which is an impure di-, tri-, ortho-phosphate. Cupric phosphate I purchased was not found to be capable of removing small quantities of hydrogen sulphide from dried coal-gas, and I have found it necessary to prepare some for use in absorption-tubes. After a few difficulties I have found a method of preparing a phosphate whose action with highly diluted hydrogen sulphide is all that could be desired. The phosphate is made from solutions of cupric sulphate and hydrogen disodium phosphate; but with these solutions it is possible to obtain many precipitates of varying composition. I have prepared some which dried at 100° give the following numbers on analysis:—

	Copper.	Phosphorus.	Cu : P.
1.....	41·18 p. c.	16·35 p. c.	5 : 4·02
2.....	40·90 „	16·24 „	5 : 4·04
3.....	33·38 „	12·54 „	4 : 3·06
4.....	42·41 „	14·50 „	3 : 2·08
5.....	39·41 „	15·36 „	4 : 3·17
6.....	39·31 „	14·47 „	4 : 3·00

The cupric phosphate for use in absorption-tubes is prepared somewhat in the following manner:—

Solutions of—

2 lbs. hydrogen disodium phosphate in 1 gallon of water, and
$2\frac{1}{2}$ lbs. cupric sulphate crystals in $1\frac{1}{2}$ gallons of water,

are mixed with vigorous stirring, and the resulting bright blue precipitate washed by decantation and then dried in a water-bath to about 100°. The material sometimes is light and powdery, sometimes hard, and then requires crushing in a mortar. Its action with hydrogen sulphide is very sharp indeed, and far more delicate than that of cupric sulphate dried at 150°.

All the **U**-tubes used in these experiments are of the new form with hollow glass ground stoppers, serving as stopcocks, the inlet and outlet connections being small pieces of glass tubing fused into the sides or the tubes. A small hole in the stopper corresponding to the hole in the side of the tube, where the small glass tubing is fused on,

makes the connection. A small turn of the stoppers closes or opens the tube. The tubes were always weighed charged with clean coal-gas, which on the same gas supply, varies but little in specific gravity.

The stoppers are lubricated with resin cerate, and with this exception are perfectly clean. A small plug of cotton-wool in each stopper prevents the mechanical carriage of fine portions of the reagents by issuing gases. Under these circumstances, I find that closed tubes charged with coal-gas suffer no appreciable variations in weight during a period of two days. These tubes are very useful indeed, and are far superior to the old form with corks.

I find that absorption-tubes charged with cupric phosphate gain in weight under the action of clean coal-gas; but the increase of weight soon reaches a limit, and the phosphate becomes "saturated." Some experiments with the 6-inch **U**-tubes, one-half charged with cupric phosphate and one-half with calcium chloride submitted to the action of a current of coal-gas dried over calcium chloride, will serve to illustrate this action, which is not due to "sulphur" compounds, as I have ascertained by special experiments.

Quantity of coal-gas used. Cubic feet.	Weight of absorption-tube. Grains.	Increase in weight. Grains.
—	1306·7	—
1·8	1307·5	0·8
2·8	1307·4	0·7
3·65	1307·4	0·7
—	1811·9	—
0·45	1812·8	0·9
2·60	1814·4	2·5
7·30	1814·5	2·6
7·65	1814·4	2·5
8·43	1814·4	2·5
—	1530·82	—
0·6	1531·77	0·95
17·52	1532·04	1·12
20·30	1532·02	1·10
21·60	1532·02	1·10
—	1529·12	—
2·0	1529·73	0·61
10·2	1530·07	0·95
12·5	1530·07	0·95

The precaution of saturating the cupric phosphate with coal-gas

must always be taken before the tubes are used, and to attain this saturation 3 cubic feet of clean dry coal-gas should be slowly passed through the tubes.

The phosphate tubes are charged in the following manner. The tubes are cleaned and dried, great attention being paid to the ground portions of the tubes and stoppers. A plug of cotton-wool is placed in the bend of the **U**-tube. This portion of the tube is almost useless where solid powdered reagents are used, and there is no practical loss of capacity by filling it with cotton-wool. Then one leg of the tube is charged with the cupric phosphate in a suitable state of subdivision, care being taken that the rough and fine portions of the powder are regularly distributed, for if all the rough portions are on one side and the fine on the other, a passage of the gas down the side where the coarse portions are takes place, and the finer portions never come into action. The other leg is charged with powdered calcium chloride. The ground portions of the tube are wiped free from dust and the stoppers, fitted with plug of dry cotton-wool in the hollow places, are lubricated with a little resin cerate and put in position. A current of dry coal-gas to the extent of 3 cubic feet is passed through, and the tubes are ready for weighing. A 6-inch **U**-tube charged in this manner will be capable of absorbing 20 grains of hydrogen sulphide, and if in the case of gas containing 10 grains of hydrogen sulphide per cubic foot, the experiments be made upon quantities of half a cubic foot, each will therefore serve for four analyses without being recharged. The calcium chloride will serve much longer.

The soda-lime tube for carbonic anhydride absorption is charged in the same manner, one half full of soda-lime and one half of calcium chloride. I have found it necessary to use the soda-lime in a moist condition, for when quite dry, soda-lime has a much feebler absorptive power for carbonic anhydride.

The requisite degree of moistness is attained by exposing it to a moist atmosphere for 12 to 18 hours. There are no inconveniences attending the use of soda-lime in this condition. These soda-lime tubes remain very constant in weight when clean pure coal-gas is passed through them, and therefore do not require saturating in the same manner as the phosphate tubes: a small quantity of dry pure coal-gas should, however, be passed through to expel air, previous to their being weighed.

A 6-inch tube charged with soda-lime in the manner above described serves for three analyses of half a cubic foot each on gas containing 10 to 12 grains carbonic anhydride per cubic foot.

In cases where ammonia also exists in the coal-gas to be analysed for hydrogen sulphide and carbonic anhydride, it will be necessary to

effect its removal before the coal-gas reaches the weighing tubes. That calcium chloride effectually removes ammonia from coal-gas I have frequently had occasion to notice, and Dibbits (*Zeits. für Analyt. Chem.*, **15**, 1876, 124) has made the same remark. But to maintain the neutrality of the calcium chloride I remove the ammonia from the coal-gas before drying, and for this purpose pass the gas through a 12-inch **U**-tube filled with broken pumice saturated with syrupy phosphoric acid.

In the drawing off of samples of coal-gas for analysis, certain precautions are indispensable, since vulcanised and iron tubing when new remove hydrogen sulphide from crude coal-gas, so that it is necessary to have the services conducting the coal-gas from the source to be tested to the absorption-tubes as short as possible, and saturated by previous use with crude coal-gas. It is further of importance to keep a tolerably quick current of gas through the iron pipe, in order to prevent the gas from getting "stale."

The iron service should be fitted with a four-way piece and three cocks. One serves to take the gas to the train of apparatus, another to be left open during the analysis, blowing gas away, and thus maintaining a rapid current in the iron pipe; the third cock can be used for other purposes, such as examination of the gas for ammonia, &c. Before making an analysis it is necessary to blow a little gas away in order to clear stale gas out of the iron service pipe, and to bring a fresh supply along.

The complete apparatus for the estimation of hydrogen sulphide in coal-gas can now be described.

The first piece in the train is the syrupy phosphoric acid tube, which can however be dispensed with in cases where the gas has been thoroughly washed free from ammonia. This tube is directly connected with the cock on the iron pipe by means of a small piece of "saturated" vulcanised tubing. The outlet of this tube is connected to a large drying cylinder filled with small pieces of calcium chloride free from alkalinity. The outlet of this drying cylinder is a **T**-piece, which carries on one arm a small piece of vulcanised tubing and screw-clamp for the purpose of blowing a little gas away before and during each experiment. The other arm of the **T**-piece is connected to the inlet of the cupric phosphate tube, which in its turn is connected with the soda-lime tube, and a gas meter connected to the outlet of the soda-lime tube completes the apparatus. The meter most suitable for the purpose is the test-meter, as used by the gas referees for the "sulphur" test. It is advisable to bring the pointer up to within a division or so of the zero by means of the key, and then to blow through until the pointer exactly covers the mark. Any error due to slackness in the gearing of index is thus avoided. Before

starting an experiment, gas should be blown away at the outlet of the drying cylinder, as well as at the cock on the iron service.

When the tubes have been weighed full of clean coal-gas, and all the pieces of the train properly joined together, the stopcocks are turned on and the gas allowed to traverse the apparatus at a moderate rate, which is often more dependent on the pressure of the gas than the will of the operator. From a quarter to one half a cubic foot per hour is a convenient rate, and one well within the limits at which the complete action of the reagents is obtained.

The quantity of gas used for each experiment is a matter of choice, and will be determined by the quantity of impurity in the coal-gas under analysis. When the required quantity of gas has passed through the tubes, the inlet stopper of the phosphate tube and the outlet stopper of the soda-lime tube are turned off, and the two tubes are taken off together, and connected in their proper order to a supply of desiccated clean gas, in order to drive the gas in the phosphate tube through the soda-lime tube. The stopper can then be turned off and the tubes weighed. Of course before weighing these tubes, they must be wiped perfectly clean and dry; but as this operation causes them to be a little light, they should be left for about five or ten minutes in the balance case before being weighed. The results corrected for temperature, &c., are best calculated to a cubic foot of clean coal-gas at 60° F. and 30 in. barometer.

In order to check the analytical results obtained with cupric phosphate, I have compared its working against that of dry mercuric oxide guarded by calcium chloride. It was before remarked that mercuric oxide loses its weight when treated with clean coal-gas, and, therefore, the results obtained are too low from this cause. I have made no correction for this error, because I do not know that the loss would be the same in cases where the mercuric oxide had been partially converted into sulphide. The numbers on the horizontal lines refer to the same sample of coal gas.

	Absorbent HgO. Grains H_2S per cubic foot of coal-gas.	Absorbent cupric phosphate. Grains H_2S per cubic foot of coal-gas.
1.....	8·09	8·65
2.....	8·55	9·26
3.....	8·24	8·81

I have further used, as a method of comparison, one mentioned by Fresenius (*Quantitative Analysis*, 1876, p. 383): "If, on the other hand, we have to determine small quantities of sulphuretted hydrogen contained in a large amount of air, &c., it is well to pass the gaseous mixture in separate small bubbles through a very dilute solution of iodine in iodide of potassium, of known volume and strength, which

is contained in a long glass tube fixed in an inclined position and protected against sunlight." In my experience very dilute solutions of iodine suffer mechanical loss of iodine when exposed and agitated with a gaseous current, and this loss becomes very considerable when the volume of gas passed through is large. In the case of coal-gas there is possibly a further loss of iodine due to hydrocarbons. In my experiments I have carefully estimated the loss in blank experiments for the exact quantities of gas used in each experiment, and also for a trifling amount of hydrogen sulphide which escaped absorption in the tube containing the iodine solution. Since the amounts of hydrogen sulphide and carbonic anhydride in crude coal-gas vary considerably in very short spaces of time, and as it was not convenient to make simultaneous experiments with the two methods on account of the very different quantities of gas used by each, the two methods were used alternately, and in this way averages were obtained that are capable of comparison together.

Iodine. Grains H_2S per cubic foot of coal-gas.	Cupric phosphate. Grains H_2S per cubic foot of coal-gas.
8·09	8·26
8·56	7·90
7·54	8·08
8·06	8·23
Average .. 8·06	8·12

I have also made some estimations on a principle similar to that used for comparing the working of hydrogen sulphide absorbents in the gas analysis apparatus. The carbonic anhydride and hydrogen sulphide were absorbed and weighed *en bloc* in soda-lime, and from a similar sample of gas the hydrogen sulphide was absorbed by cupric phosphate and the carbonic anhydride in soda-lime, according to the method above described. To be certain that gases of identical composition were being compared, I operated in the following manner:— I dried a current of crude coal-gas with calcium chloride, and then divided the current into two streams, one of which passed through a soda-lime tube guarded by calcium chloride, and the other stream through a train with cupric phosphate and soda-lime, as above described. The two estimations were simultaneous. In the annexed table the figures on the vertical columns have no necessary relation to each other, for they represent estimations made on different samples of gas. The numbers on the horizontal lines all relate to the same samples of coal-gas.

	H_2S with cupric phosphate. Grains per cubic feet.	CO_2 with soda-lime. Grains per cubic feet.	Total. Grains per cubic feet.	$CO_2 + H_2S$ with soda-lime. Grains per cubic feet.	Difference. Grains per cubic feet.
1...	8·68	7·82	16·50	16·38	0·12
2...	9·77	7·91	17·68	17·57	0·11
3...	8·79	8·13	16·92	16·58	0·34
4...	9·36	7·89	17·25	16·98	0·27
5...	9·05	8·04	17·09	16·97	0·12
6...	8·92	7·95	16·87	16·73	0·14

An inspection of this table will show that when the carbonic anhydride and hydrogen sulphide are both absorbed in soda-lime, their united weight is less than is obtained when they are separately absorbed by cupric phosphate and soda-lime. I am not able to account for the difference.

XXXIII.—*Contribution to the Chemistry of the Cerite Metals.*

By Bohnslav Brauner, Ph.D., F.C.S., Berkeley Fellow of the Owens College.

In a former paper (*Chem. Soc. J.*, Trans., 1881, 68—79), and *in extenso*, *Monatsh. Chem.*, 1882, 1—60) I described some new compounds of the cerite metals, viz., the tetrafluoride of cerium, its double salt with potassium, the pentoxide of didymium, and several double fluorides of the same metal. I likewise determined the atomic weights of lanthanum and didymium, and drew from these facts some conclusions regarding the position of this class of elements in Mendelejeff's *periodic system*.

In continuing my research in Dr. Roscoe's laboratory, I have made some new observations on the same subject, which I have now the honour to communicate to the Society.

Atomic Weight of Didymium.

The atomic weight of didymium has been determined by several chemists, but the results obtained by them differ somewhat widely from each other.

Marignac (*Ann. Chim. Phys.* [3], **38**, 148—177), in his well known

paper on didymium, published in 1853, gives the number Di = 143·7* as a mean of five determinations, varying from 143·40—143·99. Later on Hermann (*J. pr. Chem.* **72**, 385) found Di = 142·4, Zschiesche (*ibid.*, **107**, 65) Di = 142, and Erk (*Zeits. f. Chem.* [2], **7**, 106) Di = 142·48. In the year 1874 Cleve (*Bihang till Svensk. Akad. Handb.*, **2**, Nr. 8, 54), employing a large quantity of cerite, prepared some didymium, which was found by Thalén to exhibit no lanthanum lines in its spark spectrum. The determination of the atomic weight, carried on with this material, gave the number Di = 147·2, as a mean of six experiments varying from 146·81—147·39. Hillebrand's (*Pogg. Ann.*, **158**, 71) synthesis of the oxide from the metal gave the number Di = 144·78, and lastly, with a preparation that did not show any lanthanum lines in the spark spectrum, I myself found Di to be = 146·58 (mean of 146·55, 146·58, 146·60).

As the difference of more than five units between the above numbers is greater than could be attributed to mere experimental errors, I undertook experiments to decide which of these numbers represents, or most nearly approaches, the true atomic weight of didymium, and to ascertain whether pure didymium is a homogeneous body, or whether it can be split up into heterogeneous constituents, as has proved to be the case with several metals of the rare earth-group.

For this purpose a quantity of about 60 grams of crude didymium oxide, for which I am indebted to the kindness of Professor Mendelejeff of St. Petersburg, together with didymium oxide prepared by myself, were transformed into the oxalates, and these repeatedly boiled with dilute sulphuric acid, in order to remove the greater part of lanthanum. The oxalate on calcination gave an oxide, which was dissolved in dilute nitric acid, and its aqueous solution was subjected to a systematic series of fractional precipitations with ammonia, until a fairly homogeneous product was obtained. Such a preparation, however, still contained traces of cerium, which were accumulated in it, as is seen from the fact that, on destroying the oxalates by calcination, an oxide was obtained, which did not lose its brownish or rusty colour, even after continued ignition over the blowpipe in a platinum crucible. In order to purify it further, the oxide was boiled with water, to which very dilute nitric acid was added drop by drop from a burette. If only a little cerium was present, the whole of the oxides pass into solution. On adding a little ammonia, and leaving the liquid for some time on the water-bath, part of the didymium is precipitated together with cerium; for the latter metal was contained in the original solution in the form of ceric salt, which

* All atomic weights given in the present paper are referred to O = 16 and S = 32·07.—B. B.

is the least basic of all the earths present. By repeating this process several times, cerium was at last completely removed.

From the solution of didymium nitrate thus obtained, the gadolinite earths, present in small quantities, were removed by leaving the liquid for some time in contact with crusts of potassium sulphate, and precipitating in this way all the didymium as double sulphate. After filtration the last salt was boiled with caustic potash, the didymium hydroxide dissolved in nitric acid, and didymium again precipitated with potassium sulphate. The didymium hydroxide obtained after repeating this process three times, was boiled with aqueous formic acid, the insoluble precipitate ignited, and the solution precipitated with ammonia in order to remove the last traces of potassium. After dissolving the precipitate in dilute nitric acid, and eliminating the last traces of heavy metals with sulphuretted hydrogen, the solution was oxidised with bromine-water, and the didymium finally thrown down with pure oxalic acid solution. On igniting the oxalate, an oxide of a light ash-grey colour, without any brownish tint, was obtained.

In order to determine the atomic weight of didymium, a portion of the oxide was strongly ignited in a double platinum crucible; the weighed oxide carefully dissolved in pure dilute nitric acid, and after addition of the quantity of pure dilute sulphuric acid necessary for the complete saturation of the oxide, the whole was evaporated on a water-bath to dryness. The last trace of water and the small excess of sulphuric acid were partially expelled by heating the lid of the crucible, and completely driven off by carefully heating the crucible for some time to incipient redness. The atomic weight was found to be very nearly constant, both when the preparation (A) was split up into two different portions by fractional precipitation with ammonia (B and C), or by precipitation with sulphate of potassium solution (D and E).

Portion.	Weight of Di_2O_3.	Weighed sulphate.	Per cent. of Di_2O_3.	Atomic weight of Di.
A.....	1·9069	3·2593	58·506	145·36
B.....	0·7695	1·3148	58·526	145·50
C.....	0·9054	1·5477	58·500	145·31
D.....	0·9631	1·6459	58·515	145·42
E.....	1·0974	1·8749	58·531	145·53
Mean	—	—	58·515	145·42

As the different portions of the above didymium oxide do not differ sensibly among themselves in regard to the atomic weight of the

element, viz., Di = 145·42, the earth can be regarded as being pretty nearly homogeneous. But, though this number very nearly approaches the mean atomic weight, Di = 144·906, calculated by F. W. Clarke (*A Recalculation of the Atomic Weights*, Washington, 1882, 239) from numbers varying among themselves, yet it differs very sensibly from the numbers found, both by Cleve, viz., Di = 147·2, and from those obtained in my former experiments, viz., Di = 146·58, and this difference cannot be attributed to mere experimental errors. On the contrary, the true reason of this discrepancy may, as it seems, be looked for in the circumstance that an element of a higher atomic weight and of a less basic nature than didymium was eliminated from the original oxide, by precipitating the small traces of cerium present, together with a portion of didymium with ammonia.

In order to investigate this question, the few grams of didymium which served for my determination of the atomic weight (Di = 146·58), were subjected to a series of fractional precipitations with ammonia, and the least basic portions, *i.e.*, those thrown down first, were removed. The more basic portion was then used for a new atomic weight determination, and the following result obtained:—

Weight of		Per cent. of	
Oxide.	Sulphate.	Di_2O_3.	Atomic weight.
0·9750	1·6663	58·512	145·40

As this number coincides with the atomic weight of didymium found above (Di = 145·42), the supposition that the didymium, whose atomic weight was formerly found to be higher, contained an admixture of an earth with a still higher atomic weight but a less basic nature than the true didymium, becomes still more probable. The presence of this earth, which was called by me Diγ, before its true nature could be ascertained, in ordinary didymium, suffices to explain the much higher numbers found by Cleve or myself for the atomic weight of didymium. As regards the present lower number (145·42) found above, I regard it only as a maximum, which, however, as nearly as possible represents the truth, for the corresponding preparations may still have contained some of this Diγ. Still, it is remarkable that my recent number coincides with the number (Di = 145·32 when S = 32·07) which, according to Soret (*Compt. rend.*, **88**, 422), was found by Marignac for the atomic weight of pure didymium prepared from samarskite, after the separation of all foreign earths.

On the Complex Nature of Didymium.

In the following experiments I endeavoured to isolate the earth with a higher atomic weight than didymium, which always seems to

accompany it, and which I designated as "Diγ." The research was undertaken with a quantity of material much larger than that used in my former experiments.

I may be allowed to say a few words about the slight modification of the method used for the preparation of didymium from cerite.

Cerite oxides, obtained in the usual way from cerite, were dissolved in nitric acid to which some water was added, and, after evaporating the excess of nitric acid, the concentrated aqueous solution was poured into pure boiling water, when almost the whole of the cerium was precipitated in the form of insoluble basic nitrate. This was washed on the filter with boiling water, to which some nitric acid was at last added, in order to keep the liquid acid and prevent solution of the precipitate.

Pure water was used with success for precipitation instead of water acidulated with sulphuric acid (as a rule 6 c.c. of K_3SO_4 in 3 litres of water are taken for every 250 grams of the original oxides) for, even if sulphuric acid be taken, the precipitate does not consist of basic sulphate of cerium, as is generally assumed, but is a mixture of much basic nitrate with a little basic sulphate. This is easily seen from the fact that basic sulphate requires for 60 parts of CeO_2 as much as 32 parts of H_2SO_4, whereas generally only 5 parts of H_2SO_4 are taken for the precipitation of the same quantity of the oxide. (Cerite oxides contain, according to my analysis, one-half of their weight of CeO_2.) The exclusion of sulphuric acid was also found to be of advantage for the further purification of the above precipitate and the preparation of pure cerium compounds, as will be shown on a later occasion.

From the filtrate from the basic nitrate of cerium, the whole of the earths was precipitated with oxalic acid, and the oxalates were ignited, dissolved in dilute nitric acid, and evaporated to dryness. From this the cerium was removed by fusing the nitrates in a platinum basin and filtering the aqueous solution of lanthanum and didymium nitrates, slightly acidulated with nitric acid, from the insoluble basic nitrate of cerium, this process being once more repeated. From 2600 grams of cerite 1380 grams of the oxides were obtained, and this quantity yielded 700 grams of the pure mixture of lanthanum and didymium oxides, this yield being equal to the theoretical (50·7 instead of 51·3 of the original oxides).

The question now arose, how to obtain from this mixture as much pure didymium as possible. It is easily seen, that on applying the usual method, viz., precipitating one-third of the oxides in solution by ammonia and repeating the same process with the precipitated portion several times (Cleve's method), only a very little of the pure substance would be obtained, even after only a few precipitations. In

fact, no more than 1 gram would be obtained from the above quantity of 700 grams after six single precipitations, and 1 gram more for every additional series of six precipitations from the mother-liquors.

This simple calculation suggested an improved method of fractional precipitation, the principle of which is the following:—

a. From the original solution of the mixed oxides *one-half* of the contained earth is at first precipitated; then, on redissolving the precipitate, *two-thirds* of the whole lot is thrown down, and so on. In fact the greater the fraction of the less basic part precipitated, the more nearly do we approach to the pure didymium preparation; and

b. For the precipitation dilute ammonia of an approximately known strength is used, and this is added drop by drop from a burette to the liquid, kept well stirred on a water-bath. The more this ammonia is kept diluted with water the sooner do we approach the end of the operation.

In this way, after not more than eight precipitations, as much as 60 grams of very pure didymium oxide was obtained, as will be seen from the atomic-weight determination given below. The colour of the oxide was still rusty instead of grey, for the small portion of cerium still present in the original oxides had been accumulated in it. And yet it dissolved easily and completely in water to which very dilute nitric acid was added drop by drop. The last trace of cerium was removed by precipitating nearly the whole of the solution with ammonia and treating the precipitated basic nitrate with hydrogen dioxide on the water-bath in order to convert the whole of the cerium into the ceric salt. After some time the precipitate was dissolved in very dilute nitric acid until only a little of the precipitate remained behind; a small quantity of dilute ammonia was then added, and the brownish precipitate, consisting mostly of basic nitrate of cerium, together with a trace of iron, was separated by filtration without washing.

Didymium nitrate prepared in this way still contains considerable quantities of yttria and other gadolinite earths, for an atomic-weight* determination, carried on with a part of the precipitated oxide, gave the very low number $R''' = 137{\cdot}8$. In order to remove yttria, &c., from this small part of the whole preparation, the dilute aqueous solution of the sulphate was treated with sulphate of potassium, the precipitate boiled with caustic potash, the hydroxide gradually added to boiling aqueous formic acid, and the precipitate, after ignition, sub-

* I may be allowed to speak of an "atomic weight of a mixture of earths," or of a "variation of the atomic weight," meaning by atomic weight the relative quantity of earth-metal or radical of an earth, which combines with 24 ($= 16 \times \frac{3}{2}$) parts of oxygen.—B. B.

jected to the treatment with formic acid twice more. Only after this treatment was the preparation found to consist of didymium with an atomic weight of Di = 145·9.

The atomic weight of didymium in this preparation is higher by 0·5 than that of the purest substance above (viz., Di = 145·4), and experiments were therefore undertaken to split up this preparation into several parts, especially into the true didymium and the other constituent called "Diγ," the presence of which in ordinary didymium tends to raise its atomic weight. This was done by dropping dilute aqueous ammonia into the neutral warm solution containing didymium, together with the earths of the yttria-group, in the form of nitrates, and precipitating the whole of the earth in solution, with the exception of 3 grams of the most basic earth, which were left in the filtrate. This mode of operation, viz., one precipitation, corresponds to one series of decompositions of the nitrates by heat, as commonly used for the separation of the gadolinite earths. The precipitated part was dissolved in dilute nitric acid and treated in the same way 16 times.

Let us call the first filtrate I*a*, and the following three I*b*, I*c*, I*d*. All these four filtrates were put together, precipitated with oxalic acid, and so the fraction I obtained. The next four filtrates yielded fraction II; then came fraction III, fraction IV, and the least basic residue was called fraction V. The salts obtained from the fractions I, II, and III were of a beautiful pink colour, that from fraction IV was paler, and fraction V was white, and consisted chiefly of earths of the yttria-group. As not only fraction V, but all the other fractions, contained larger or smaller quantities of earths of the yttria-group, the following method was used for their separation:—

To a boiling aqueous solution of pure formic acid (prepared by Kahlbaum) the ignited earth was added in small quantities, and thus an insoluble precipitate, consisting chiefly of didymium formate, was obtained, the gadolinite earths remaining chiefly in solution. After filtering, and washing the precipitate three times with small quantities of cold water, it was dried, ignited, and the oxide twice again treated in the same way with formic acid.

This purification by means of transforming the oxides into the formates, &c., was carried on with each of the five fractions separately. At the end of all the above extremely elaborate processes, five portions of the oxides, corresponding with the five fractions, were obtained. After dissolving in nitric acid, precipitating with oxalic acid, and igniting, the pure oxides were prepared, and these were used for the atomic weight determinations. The following table contains the results obtained:—

Fraction No.	Weight of		Per cent. of R_2O_3.	"Atomic weight."
	Oxide.	Sulphate.		
I.....	1·2139	2·0802	58·355	144·32
II.....	1·8256	3·1218	58·479	145·16
III.....	1·3995	2·3919	58·510	145·39
IV	1·3285	2·2611	58·755	147·10
V.....	0·7645	1·2942	59·071	149·35
	0·5768	0·9762	59·086	149·46

It is easily seen from these numbers that didymium with an atomic weight of 145·9, which was formerly considered to be pure, is not a simple body, but a mixture of earth-metals, the atomic weights of which vary at least from 144·3 to 149·4, and into which it can be split up by a systematic series of fractional precipitations with ammonia. It should be remembered that the above mixture of earths yields very difficultly soluble formates, and the earths belong therefore to the cerite group of metals, and that the gadolinite metals, forming easily soluble formates, and occurring also in cerite, were collected in the filtrates obtained on repeatedly treating the single fractions with formic acid. The nature of these earths will be described further on.

Examination of the Different Constituents of Didymium.

Let us begin with fraction V, having the highest atomic weight of all the portions, viz., R = 149·4. This fraction might be expected to contain the hypothetical earth, termed provisionally "Diγ," which when present in ordinary didymium raises its atomic weight. In order to study its nature, the absorption spectrum of the aqueous solution of the sulphate was examined. As this liquid was found to exhibit the absorption-bands of samarium, it may be well to mention that, according to the researches of Lecoq de Boisbaudran and Soret, solutions of samarium possess the following absorption-bands in the visible part of the spectrum. Beginning with the line in the red end (symbol Sm_1), we have—

Wave-length in $\frac{1}{1000000}$ *mm.*

Band : Sm_1.	Sm_2.	Sm_3.	Sm_4.	Sm_5.	Sm_6.	Sm_7.	Sm_8.
559	500	489	480	463·5	419—415	408—406	400·75

The solution of the earth still contains some didymium, for the principal bands of this element were easily distinguished in its spec-

trum. Of the samarium bands, only those in the violet part of the spectrum were visible in the dilute solution.

When a solution of didymium containing samarium in somewhat larger quantities is diluted to a certain degree, and compared with a solution of didymium of the same concentration, *i.e.*, when the intensity of the didymium bands in the yellow and green part of the spectrum is the same in both solutions, it exhibits a peculiar phenomenon. Whereas in pure didymium solution the bands $\lambda = 482{\cdot}5$, $475{\cdot}8$, $469{\cdot}1$, and 444 are still distinctly visible, in the mixed solution of didymium and samarium the first three lines disappear completely, and the band $\lambda = 444$ becomes much fainter. Though a similar phenomenon has been already observed by Delafontaine (*Compt. rend.*, **87**, 634), Lecoq (*ibid.*, **88**, 322), and Soret (*ibid.*, **88**, 422; Archives [3], **4**, 261), in the spectrum of didymium from samarskite, it has not yet been explained. Delafontaine, however, is of the opinion that didymium from cerite contains a new element, characterised by those bands which are not found in didymium from samarskite.

I have further observed that on gradually concentrating the above mixed solution of didymium and samarium exactly in the same place of the spectrum in which the missing didymium bands ought to be found, a strong and wide double absorption-band, namely Sm_3 and Sm_4, begins to make its appearance, covering up the three didymium bands. On further concentrating the solution, this double band becomes quite black, and even now the three lines of didymium are invisible, though the last metal is present in a pretty concentrated state. Again, on gradually diluting the mixed solution, the intensity of the double band of samarium will decrease, and at last, though with difficulty, only a wide minimum of transmission of light will be observed in that part of the spectrum. In spite of its faintness it is strong enough to render the three lines of didymium invisible in cases where they would be visible if didymium were present alone.

I think that the disappearance of the three didymium lines is thus satisfactorily explained, at any rate in the case with which I had to deal.

In the concentrated solution of the above impure sample of samarium, the following absorption-bands are seen:—First, the samarium bands, Sm_1, Sm_2, $Sm_3 + Sm_4$ (which both form together one wide band), Sm_5, Sm_6, Sm_7, and Sm_8 (the last was only observed in sunlight), then some of the didymium bands, and at last two holmium bands ($\lambda = 640$ and 536), and three erbium ones ($\lambda = 653$, 541, and 450).

The quantity of didymium present in this sample of samarium sulphate was estimated by preparing a didymium solution of known strength, and diluting it until the yellow and green didymium bands

in the absorption spectrum of both reached an equal intensity. This quantity was found to be equal to 25·2 per cent., and from this the atomic weight of samarium was calculated to be Sm = 150·7.

The atomic weight of samarium has not yet been determined by any chemist, but, according to Marignac (*Archives des Sciences Phys. Nat.*, Mai, 1880) it has the same absorption spectrum as Marignac's new earth-metal, $Y\beta$. The only difference between the two earth-metals is that the salts of $Y\beta$ are of a yellowish colour, whereas those of samarium are colourless. The atomic weight of $Y\beta$ is 149·4 (in maximum), whereas that of samarium of my preparation, evidently in maximum, is Sm = 150·7. This difference is most probably due to the admixture of small quantities of erbium (Er = 166) and holmium (Ho = 162 about), and even the possibility of an admixture of one or more earths with a higher atomic weight is not completely excluded.

Although no chemist has yet prepared samarium compounds in the pure state, there is no doubt that this element has an independent existence, as it possesses a characteristic absorption spectrum, whilst the number Sm = 150 very nearly approaches its true atomic weight.

Examination of Fraction IV.—The mixture of earth-metals contained in this fraction has an atomic weight of 147·10. Though it consists principally of didymium, yet it contains no small quantity of ammonium, as is seen by the presence of the following bands of this metal:—Sm_4 (feeble), Sm_5 (feeble), Sm_6 and Sm_7 (a little stronger), Sm_8 (pretty strong).

In order to observe the band Sm_8 of the wave-length = 400·75, which is situated almost at the end of the visible violet part of the spectrum, direct sunlight must be passed through the solution into the spectroscope. The light of the electric arc does not answer the purpose, for it usually shows by itself in the same place in which the band $\lambda = 400{\cdot}75$ is situated, a dark absorption-band, due, as it seems, to impurities in the carbon poles. Incandescent electric light (*e.g.*, that of an Edison lamp) gives a better result, but sunlight best answers the purpose, as the smallest traces of the band Sm_8, and, therefore, of the metal itself, can be easily distinguished and detected in this way.

In fraction III, atomic weight = 145·39, only the band Sm_8 could be seen, and it was distinct though feeble.

In fraction II, atomic weight = 145·16, the band was only very feeble; and in fraction I it was scarcely visible.

As the fractions II and III, 18 grams in weight, are situated in the middle of the whole series of decompositions, and as their atomic weight is very nearly identical with that of the purest didymium pre-

pared formerly, viz., Di = 145·4, they may be regarded as containing the purest didymium of the whole series of fractions and as identical with the purest preparation. This in its turn was tested spectroscopically for samarium, but as the band Sm_β could only be distinguished in it with great difficulty, it may be regarded as practically free from samarium.

The number Di = 145·2—145·4 may therefore be assumed to represent as nearly as possible the true atomic weight of didymium, but it must be shown by further experiments whether this number will be sensibly affected or not when the last trace of samarium has been eliminated, and how far the properties of pure didymium compounds will differ from those which have as yet been described.

Gadolinite Earths from Cerite.

The question whether cerite contains earths of the yttria-group, as well as those of the cerium-group, has not yet been answered satisfactorily, for whereas yttria was found in cerite by Esk (*Zeit. f. Chem.* [2], **7**, 107), Bunsen could detect neither yttria nor erbia in "a few centigrams" of the mineral before the spectroscope; and from this fact some chemists have drawn the conclusion that this class of earth-metals is totally absent from cerite.

It has been stated above that the yttrium metals were accumulated in fraction V, which was the least basic of all. In fact, on treating the 60 grams of didymium oxide containing no earth of greater basicity than didymium, by formic acid in portions, not less than 12·2 grams of earths were obtained from the soluble formates. The 640 grams of more basic earths, which were put aside from the original 760 grams of the mixture of earths, undoubtedly contain another quantity of gadolinite earths. The atomic weight of the above mixture of earths was 114·5. This low number clearly shows that yttria must have been present in this mixture in large quantities, and this was confirmed on examining the spark spectrum of the hydrochloric acid solution of the earth, in which the characteristic group of lines in the red belonging to yttria was seen with great brilliancy. As regards terbia, it is known to accompany yttria in almost all minerals, and it might therefore be expected to be present in cerite. Moreover, the deep orange colour, characteristic of terbia, which I found the earth from the less soluble formates to possess, renders the occurrence of terbia in cerite still more probable. Holmia was found to be present by two of its characteristic absorption-bands (λ = 641 and 536), Thulia by one band (λ = 684), and Erbia by all its eight bands.

The above experiments prove that the principal gadolinite earths

are contained in cerite, in addition to those of the cerium-group, though of course not in large quantities, and that oxide of didymium if prepared in the usual way as the least basic of earths present in cerite, is not a homogeneous body, but a mixture of earths.

The investigation of the cerite earths, which were left untouched in the present memoir, is in progress, and its results will form the object of another communication.

XXXIV.—*Some Compounds of Antimony and Bismuth containing two Halogens.*

By R. W. Atkinson, B.Sc. (Lond.), F.I.C.

Amongst so-called "double-salts," one of the best characterised is that produced from antimonious chloride and potassic chloride. Discovered by Jacquelaine about 40 years since, it has been followed by other salts built up in a similar manner, though beyond a more or less detailed description of their physical properties no attempt seems to have been made to subject them to such an examination as it is now universally the custom to submit organic compounds to for the purpose of ascertaining their constitution. Such an examination ought to be synthetic as well as analytic, but evidently little information could be gained by combining two such salts as potassic chloride and antimonious chloride, for the reason that the chlorine in the former salt could not be distinguished from that in the latter after combination had taken place; in order, therefore, to be able to distinguish the halogen in combination with the potassium, from that combined with the antimony, I used chlorine in the one case, and bromine in the other. By this means, on the theory of a molecular combination between the respective salts, two distinct compounds ought to be produced, viz., (1) $SbCl_3.3KBr$, and (2) $SbBr_3.3KCl$. On mixing together antimonious chloride and potassic bromide in the proportions in No. (1), adding just sufficient water to ensure solution, and slowly evaporating over oil of vitriol, yellow rhombic pyramids were obtained, possessing the composition $SbCl_3Br_3K_3 + 1\frac{1}{2}Aq$.

Similarly, by mixing together antimonious bromide and potassic chloride in the proportions required for (2), under like conditions, yellow pyramidal crystals were obtained, which, from the crystallographic examination kindly undertaken by Mr. R. H. Solly, of the Mineral Museum, Cambridge, are identical with the former. The

formula found also was identical, viz., $SbCl_3Br_3K_3 + 1\frac{1}{2}Aq$, from which we may conclude that the same body is produced in both cases. Their chemical behaviour also is the same. Over calcic chloride they effloresce at ordinary temperatures, and finally lose the whole of their water of crystallisation; at a slightly elevated temperature they lose their water very readily. In ordinary air they gradually deliquesce to a clear yellow liquid. The crystals also dissolve in a small amount of water, giving a solution when saturated, having a specific gravity of 1·9, and containing 120·5 grams in 100 c.c. A larger quantity of water decomposes the salt, forming a mixture of SbOCl and SbOBr, and on the addition of a still larger amount of water a mixture of $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$ is formed. In the former case the mixture consists of the compounds in equal molecular proportions, but in the latter the proportions are not quite equal, more chlorine being removed than bromine.

Strong hydric chloride dissolves the crystals at first, and almost immediately deposits a crop of crystals of potassic chloride, the solution doubtless containing the hydrogen salt, $SbCl_3Br_3H_3$, which, however, I have not succeeded in isolating.

The action of heat upon the crystals is of considerable interest. The dried salt, which is of a pale lemon-yellow colour, on heating to 100° C., becomes darker in colour, but on increasing the heat to between 200—300°, it loses its yellow colour, and leaves a white mass, whilst antimonious fumes escape. The loss in weight is a little more than 50 per cent., and the residue contains chlorine and bromine in equal atomic proportions, so that the antimony in being volatilised has carried away with it one-half of the chlorine and one-half of the bromine. Taken in connection with the amount of water in the crystals, we must give them at least the formula $Sb_2K_6Cl_6Br_6 + 3Aq$.

Nicklès (*Ann. Pharm.*, **40**, 191) has described a chlorobromide of bismuth and ammonium formed by adding bromine to powdered bismuth, suspended in a solution of ammonic chloride. He attributed to it the formula $Bi(Cl_5Br_5)N_2H_8 + 5H_2O$, which, however, does not agree so well with his analytical data as a formula similar to the one above given, viz., $BiCl_3Br_3(NH_4)_3 + H_2O$. I have not prepared this salt, but I have little doubt but that it corresponds exactly with the antimonio-potassic chloro-bromide described above. I hope to be able to compare them on a future occasion.

The following are the analytical numbers obtained, but on account of the impossibility of freeing the crystals completely from the mother-liquid, they are not so closely concordant as might be desired. The numbers for bromine and chlorine refer to the dried salt.

	1.	2.	3.	4.	Mean.	Theory.
Bromine....	41·49	40·80	—	—	41·14	41·13
Chlorine....	17·82	18·11	—	—	17·96	18·30
Water	4·70	—	4·60	4·80	4·70	4·40

From the facts above communicated we must conclude, I think, that in the molecule $(SbCl_3Br_3K_3)_2$, there is no evidence of any grouping into two parts, as the theory of molecular combination supposes. If it were otherwise we should expect to find that on heating (no fusion taking place) the residue would consist wholly of potassic chloride *or* potassic bromide, as the case might be, not of a mixture of the two in molecular proportions. This remark also answers sufficiently the objection that by the act of solution a redistribution of elements takes place, and that therefore we must obtain the same compound from whichever pairs we start. Granting that it were so, the crystals resulting would have one or other of the two constitutions—

$$SbBr_3.3KCl \text{ or } SbCl_3.3KBr,$$

and on heating either all the bromine or all the chlorine would be driven off, not one-half of each.

In making the above experiments I obtained combinations in other proportions, which have not been examined crystallographically, owing to the difficulty of getting sufficiently bright surfaces.

1. $Sb_2Cl_6Br_3K_3 + 2Aq$.—This compound was deposited from a solution of the crystals previously described, containing a small excess of antimonious chloride. The crystals apparently belong to the rhombic system, and are much lighter in colour than the former. The following gives their composition:—

		Theory for $Sb_2Cl_6Br_3K_3 + 2Aq.$
Bromine.....	28·05	28·37
Chlorine.....	25·02	25·17
Water	5·40	4·25

2. $SbCl_3BrK + H_2O$.—From a mixture of two molecules of antimonious chloride with three of potassic bromide in saturated solution, successive crops of crystals were obtained, the earlier ones being contaminated with crystals of potassic bromide, and only towards the last were they found to be free from that salt. The earlier crystallisations gave numbers leading to the formula $5SbCl_3.6KBr + 8H_2O$, but these were probably not homogeneous, though no difference could be detected between the different crystals. The later crystals were pale-yellow octahedra, having the following composition:—

		Theory for $SbCl_3BrK + H_2O.$
Bromine.....	22·62	22·01
Chlorine.....	29·23	29·30

In their composition they resemble the salt formed from antimonious iodide and potassic iodide, which has the formula $SbI_4K + H_2O$.

Bismuth Compound.

Attempts were made to obtain a bismuth salt similar to the antimony one first described, viz., from $BiCl_3 + 3KBr$, and from $BiBr_3 + 3KCl$, but hitherto without success. The following new salt was obtained during the experiments, but the crystals have not been examined crystallographically, further than to ascertain that they belong to the rhombic system.

3. A solution of bismuthous bromide in a saturated solution of potassic chloride, after standing in a desiccator over oil of vitriol, deposited thin pale-yellow lozenges. An analysis gave the following results:—

		Calculated for	
	Found.	$BiCl_3Br_2K_2 + 1\frac{1}{2}H_2O$.	$BiCl_3Br_2K_2 + 2H_2O$.
Bromine.....	27·50	27·60	27·20
Chlorine.....	18·40	18·38	18·10
Water.....	5·60	4·66	6·10

The formula with $1\frac{1}{2}$Aq is more probably correct, the crystals doubtless retaining a little water.

A second crop of crystals obtained from the same solution had a darker yellow colour and a stumpy prismatic appearance, but, except that they were slightly contaminated with some potassic bromide, they gave similar numbers:—

	1.	2.	Mean.	Theory for $BiCl_3Br_2K_2 + 1\frac{1}{2}$Aq.
Bromine	28 64	28·10	28·37	27·60
Chlorine	18·40	18·10	18·25	18·38
Water	4·94	—	4·94	4·66

In conclusion I have much pleasure in recording my obligations to Dr. Williamson, For. Sec. R.S., for his kindness in permitting me to carry out these experiments in the Laboratory at University College, and also for much valuable advice during the course of the investigation.

XXXV.—*Crystallographic Examination of the Crystals of Antimoniopotassic Chlorobromide.*

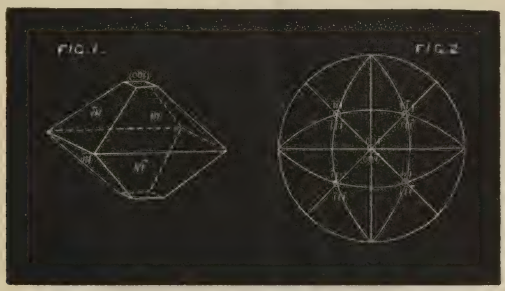
By R. H. Solly, Esq., Cambridge.

The crystals of the two salts in the solutions marked A and B—

A ..... a solution from $SbBr_3 + 3KCl$
B ..... „ „ $SbCl_3 + 3KBr$,

have been carefully examined. More than 20 crystals were measured; some were measured twice after an interval of a fortnight. The bright faces gave the same angles, but the dull and rough ones varied. Only a very few of the crystals gave distinct reflections of the bright signal, the best angles range from 62·25—62·34°; 62·29° was found three times on the A crystals, and five times on B crystals; 62·29° is the angle used to calculate the element, as it was obtained thrice from very good faces. The face (001) was found well developed on two crystals in B solution. These crystals are therefore crystallographically similar, both crystallising in the tetragonal system, and exhibiting similar development. There is no apparent cleavage.

System tetragonal. Common form (111), but sometimes in combination with (001), Fig. 1.



	Angles calculated.	Angles found.		
$(111)(\bar{1}11)$	= 62·29°	62·25°	62·29°	62·34°
$(111)(1\bar{1}1)$	= 62·29	62·25	62·29	62·34
$(111)(11\bar{1})$	= 85·39	85·26	85·40	85·58
(111)(001)	= $47·10\frac{1}{2}$		47·15°	

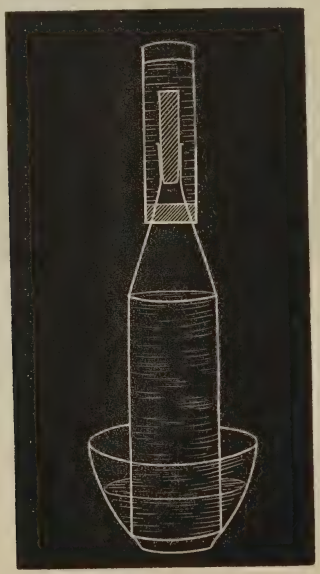
tan E = $37·20\frac{1}{3}$ = 0·762882.

XXXVI.—*On the Gases evolved during the Conversion of Grass into Hay.*

By Percy F. Frankland, Ph.D., B.Sc., Demonstrator of Practical Chemistry in the Normal School of Science, South Kensington, and F. Jordan, F.C.S.

That a high temperature is rapidly acquired by a stack of freshly cut and imperfectly dried hay is a fact so well known to farmers and others, that it appeared to us of some interest to ascertain the nature of the gases evolved in this process. We have also endeavoured to determine how the evolution of gas is influenced by the conditions under which the grass is placed.

The apparatus employed was of a very simple nature. In order to isolate the grass and the gaseous products obtained from it, a quantity (usually 5 grams) of finely-cut grass was in each case imprisoned in a glass tube standing over mercury. The tubes found most convenient for the purpose were small retort-adapters; the grass being introduced at the wide extremity, which was then placed in a mercury-trough, and the greater part of the air removed by completely immersing the tube in the mercury, and then, whilst in that position, closing the smaller extremity by means of an india-rubber plug surrounded by a mercury-cup, as shown in the figure.



When the grass was to be immersed in an atmosphere other than air, the tube containing the grass was placed in a mercury-trough and a current of the gas passed through by attaching an india-rubber tube to the smaller extremity, and allowing the escaping gas to bubble out from the larger aperture. The current of gas was usually passed for several hours to insure all the residual air contained in the grass being displaced. The gas evolved from the grass could afterwards be transferred by removing the india-rubber stopper under mercury, and allowing the gas to bubble into a test-tube filled with mercury placed above for its reception. The analysis of the gases was performed in the latest modification of Frankland and Ward's gas apparatus.

In an Atmosphere of Air.—The tube containing grass and air was kept at the prevailing temperature, about 15° C. The gas in the tube was analysed after three days, and the further quantity evolved after standing 30 days:—

	3 days.	30 days.
CO_2	46·35	85·33
O	0·07	0·00
N	53·58	14·67
	100·00	100·00
Volume ..	3·0 c.c.	4·0 c.c.

Thus in a space of three days practically the whole of the oxygen had been removed from the air with which the grass was saturated, whilst after 30 days a further quantity of carbonic anhydride was evolved, the oxygen for which must have been obtained from the substance of the grass, inasmuch as the atmosphere surrounding the grass was destitute of oxygen. The nitrogen in the air necessarily precludes the possibility of drawing any inference as regards the evolution of nitrogen from the grass.

In an Atmosphere of Carbonic Anhydride.—A tube with grass from which the air had been displaced by carbonic anhydride, as before described, was left at the temperature of the air (about 15° C.), and the gas evolved, removed, and analysed after three days, and then again after 30 days. The volume and composition were—

	3 days.	30 days.
CO_2	100·00	100·00
Volume	4·5 c.c.	2·0 c.c.

Another tube prepared in the same way was exposed for six hours a day to a temperature of 36° C. for three days, and then left at the temperature of the air.

The volume and composition of the gas were—

	3 days.	28 days.
CO_2	97·96	98·75
Other gases..	2·04	1·25
	100·00	100·00
Volume	9·0 c.c.	16·7 c.c.

Two similar tubes were prepared as above, and one exposed to daylight, and when possible sunlight, for 14 days, whilst the other was kept for the same space of time in darkness. The composition and volume of the gases evolved were—

	In light.	In dark.
CO_2.....	96·92	97·23
H	0·41	1·86
Other combustible gas..	0·48	0·12
N	2·19	0·79
	100·00	100·00
Volume	5·0 c.c.	13·0 c.c.

From the above it appears that in an atmosphere of carbonic anhydride the gas evolved from grass is almost pure carbonic anhydride, moreover that the volume of gas given off at 36° C. is greater than at 15° C., and less in light than in darkness. The latter must be accepted, however, with some reservation, inasmuch as we have repeatedly found that tubes prepared in apparently precisely the same manner and exposed to like conditions often yield very different volumes of gas.

In an Atmosphere of Oxygen.—A tube was, in the first place, prepared containing grass from which the air had been displaced by oxygen. The whole of the evolved gas was removed for analysis after the tube had stood for 7, 8, 11, and 23 days, the following results being obtained:—

	7 days.	8 days.
CO_2.....	77·47	90·08
N	22·53	9·92
	100·00	100·00
Volume	6·2 c.c.	3·3 c.c.

	11 days.	23 days.
CO_2.....	96·64	98·68
H	1·92	0·50
Other combustible gas..		0·31
N	1·44	0·51
	100·00	100·00
Volume	4·0 c.c.	3·2 c.c.

The above analyses show that only at the outset of the experiment was the grass surrounded by an atmosphere of oxygen, since already at the end of seven days the whole of this gas had been removed. The analyses further show that after the removal of oxygen from the atmosphere, the evolution of nitrogen practically ceases, the 9·92 per cent. found in the second portion of gas being certainly in great part, if not altogether, due to the residual gas still adhering to the grass after the removal of the first portion.

In order to ascertain whether the evolution of nitrogen would continue if the grass were always supplied with oxygen, a tube was prepared as before, and each time, after removing the gas for analysis, a quantity of pure oxygen was passed into the tube so as to leave it half full. The portions of gas successively removed yielded on analysis the following results, in which the percentages are given after deducting the free oxygen:—

	3 days.	5 days.	17 days.	32 days.	89 days.	109 days.
CO_2	75·67	76·17	85·77	90·80	92·40	91·59
H and combustible gas	2·78	1·27	2·70	2·76	0·70	2·49
N	21·55	22·56	11·53	6·44	6·90	5·92
	100·00	100·00	100·00	100·00	100·00	100·00

In an atmosphere of oxygen the proportion of nitrogen liberated, although greatest at the outset, is thus still very considerable even after the lapse of several months.

In an Atmosphere of Hydrogen.—No diminution in the volume of gas liberated from grass takes place when the latter is surrounded by an atmosphere of hydrogen. Thus from a tube containing 5 grams of grass, no less than 8·5 c.c. of gas were liberated during three days, the tube being kept at a temperature of 36° C. for six hours each day. The composition of the gas from another tube was:—

CO_2	21·11
H	76·62
Other combustible gas	0·58
N	1·69
	100·00

It thus appears that the atmosphere with which the grass is surrounded has but little influence either upon the volume or the composition of the gas. The grass in every case undergoing a rapid process of oxidation, in which it speedily removes all the oxygen

from the atmosphere with which it is surrounded, and in the absence of any oxygen in the free state with which to combine, considerable volumes of carbonic acid are notwithstanding produced at the expense of the combined oxygen present in the grass. When free oxygen is present in the atmosphere surrounding the grass, the gas evolved contains a considerable proportion of nitrogen. This result agrees with those obtained by Lawes, Gilbert, and Pugh, who, in their classical researches upon the assimilation of nitrogen by plants (*Phil. Trans.*, Part II, 1861), proved that when certain vegetable matters, such as wheat, bean seeds, turnips, &c., were exposed to an atmosphere containing free oxygen, nitrogen was evolved. In all cases carbonic anhydride is the chief product of decomposition, whilst hydrogen and hydrocarbons appear in only very small quantity.

Decomposition of Grass under Water.

When grass is allowed to decompose under water, generally much larger volumes of gas than those recorded above are disengaged, and the composition of this gas is characterised by a notable percentage of hydrogen.

The tubes containing the grass were prepared in the same way as before, only that the grass was first soaked in distilled water, and the dissolved air removed by exhaustion with the Sprengel pump. The following results were obtained with one tube; the gas being removed for analysis after 3 and after 30 days:—

	3 days.	30 days.
CO_2	84·63	93·04
O	0·13	0·00
H	6·90	4·15
Other combustible gas.	2·51	0·98
N	5·83	1·83
	100·00	100·00
Volume	15·0 c.c.	10·5 c.c.

Again, with another tube the following results were obtained:—

	3 days.	4 days.
CO_2	87·66	84·41
H	8·75	9·17
Other combustible gas.	0·71	0·27
N	2·88	2·15
	100·00	100·00

and with another after standing 17 days—

CO_2	90·09
H	8·16
Other combustible gas	0·71
N	1·04
	100·00

Tubes were also prepared containing grass immersed in a $1\frac{1}{2}$ per cent. solution of phenol, and a 1 per cent. solution of mercuric chloride respectively, but in neither case was any gas evolved. A tube containing grass immersed in water was exposed to the heat of a steam-bath for several hours, and this yielded no gas, although the tube was kept for several weeks. Thus the evolution of gas is evidently dependent upon the presence of low forms of organic life, and in the water taken from the tubes, the microscope always revealed numerous bacteria. As this water also gave an acid reaction with test-paper, a further experiment was made on a larger scale to determine the other products of the fermentation.

For this purpose about 7 lbs. of grass were introduced into a capacious retort and covered with recently boiled water. During the first three days the contents of the retort were exhausted with a water-pump, after which the retort was fitted with a delivery-tube, and the gas subsequently evolved was collected over water. In the course of 22 days about 1 litre of gas had collected, which on analysis was found to contain 20 per cent. of hydrogen.

After 27 days the liquid was poured off and distilled with phosphoric acid to a small bulk. The distillate, containing the volatile acids, was treated as below. The residue remaining in the retort was filtered, and the filtrate repeatedly shaken out with ether in order to extract the fixed organic acids. The ethereal extract was then diluted with water, an excess of precipitated baric carbonate added, and the liquid heated to volatilise the ether. After filtering off the excess of baric carbonate, the filtrate was evaporated to dryness on a water-bath, and the residue, after being washed with alcohol, was dried at 130° C., and the barium determined:—

0·2255 gram of barium salt gave 0·1655 gram $BaSO_4$, equivalent to 43·14 per cent. Ba.

Baric lactate.	Ba per cent. calculated.	Found.
$(C_3H_5O_3)_2Ba$.	43·49	43·14

The distillate mentioned above, and containing the volatile acids, was divided into two equal parts, one of which was then exactly neutralised with caustic potash. After again uniting the two portions,

the mixture was distilled nearly to dryness. The acid distillate was treated with an excess of freshly precipitated baric carbonate, and, after filtration, the solution was evaporated down, and the residue recrystallised. The crystals were dried at 130° C., and the barium determined :—

I. 0·4540 gram of barium salt gave 0·3757 gram $BaSO_4$ = 48·65 per cent. Ba.

II. 0·6080 gram of barium salt gave 0·5028 gram $BaSO_4$ = 48·61 per cent. Ba.

		Found.	
Baric propionate.	Ba per cent. calculated.	I.	II.
$(C_3H_5O_2)_2Ba$.	48·41	48·65	48·61

Although the barium salt thus agrees in its percentage of barium with baric propionate, there is just the possibility that it might have been a mixture, in the proportion of their molecular weights, of baric acetate and baric butyrate; unfortunately sufficient material was not at our disposal to decide this point.

The residue left in the retort in the last distillation was treated with phosphoric acid and distilled almost to dryness. The acid distillate was treated with an excess of baric carbonate, filtered, the filtrate evaporated down, and the residue obtained recrystallised. The crystals were dried at 130° C., and the barium determined :—

0·2950 gram of barium salt gave 0·2674 gram $BaSO_4$ = 53·28 per cent. Ba.

Baric acetate.	Ba per cent. calculated.	Found.
$(C_2H_3O_2)_2Ba$.	53·73	53·28

The products of fermentation which accompany the evolution of gas described are thus acetic, lactic, and probably propionic acids.

From these experiments it appears :—

(1.) That comparatively dry grass soon evolves considerable quantities of gas consisting almost wholly of carbonic anhydride, and accompanied by mere traces of hydrogen and hydrocarbons.

(2.) That the evolution of gas takes place with almost equal rapidity in atmospheres composed of air, carbonic anhydride, oxygen or hydrogen; and that excepting when the atmosphere contains oxygen, in which case a notable proportion of nitrogen accompanies the carbonic anhydride, the composition of the gas evolved is much the same.

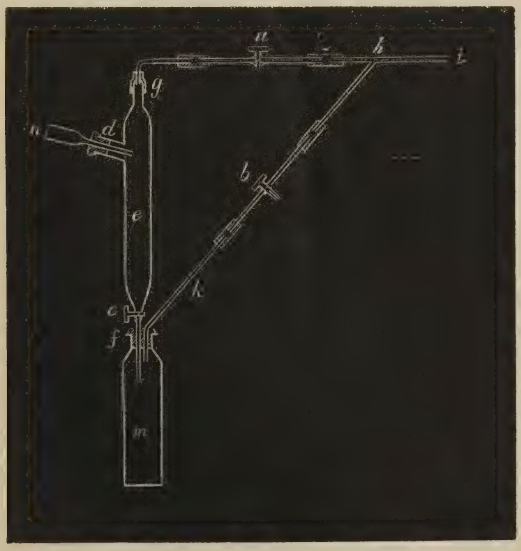
(3.) That when the decomposition of grass takes place under water,

large volumes of gas are evolved which are characterised by the presence of a notable proportion of hydrogen. This hydrogen is doubtless due to the lactic fermentation induced by bacteria; acetic, lactic, and probably propionic acids, together with bacteria, being found in the water in which the grass was immersed.

XXXVII.—*Note on an Apparatus for Fractional Distillation under Reduced Pressures.*

By L. T. Thorne, Ph.D.

In distilling *in vacuo*, or under reduced pressure, the chief difficulty is usually the removal of the various fractions without breaking the continuity of the distillation. It is believed that the apparatus of which a sketch is annexed, will be found to be an improvement on those now in use.



The receptacle *e* is a tube about 10—12 cm. long, and 10—12 mm. in diameter, closed below with a stopcock *c*, the lower delivery tube of

which is drawn out to a narrow quill tube about 4 cm. long.* Near the top of *e* is a tubulure *d* to admit the end of the condenser; the upper end is somewhat narrowed for convenience in making connection with the stopcock *a*. The other end of the stopcock *a* is connected with a **T**-piece *h*, the outlet *i* of which communicates with the exhausting pump, and the third limb with the *three-way cock b*. To the other end of *b* is attached the tube *k*, the lower end of which is slightly drawn out and bent parallel with the quill end of *c*. These two tubes are then passed through a doubly bored caoutchouc stopper *f*, on which is fastened the bottle, test tube, or other receiver *m*.

The drawn-out end of the condenser or cooling tube *n* is fitted air-tight into the tubulure *d* by means of a cork, the end of the tube projecting well into *e*: the outlet *i* is connected with the vacuum pump, stopcock *a* being open, and the three-way tap *b* so arranged that *h* and *k* are in communication, and the pump is set in action. In this way the whole apparatus is exhausted, and the distillation is then commenced. As soon as the first fraction has passed over into *e*, or that receptacle has become full, stopcock *c* is opened, when the distillate at once flows into *m*. Should the distillate be at all viscid and not flow easily, stopcock *a* is closed, and the exhauster acting through *b* and *c* assists gravitation: *c* is then closed again, and if it is wished to change the receiver *m*, the three-way tap is so turned that *m* is put in communication with the air while the bore leading to *h* is closed. When a fresh receiver *m'* has been adjusted, *a* is closed for a few seconds, and *b* turned so as to place *h* and *k* again in communication, and when *m* is exhausted *a* re-opened. In this way any number of fractions may be collected without for a moment stopping the distillation, and by selecting *f* of a suitable size, the distillate may, if desirable, be collected directly into the vessel in which it is afterwards to be used.

In practice it is found that owing to the slight irregularity in working of the exhausting pump (especially where a water-pump is used), it is very advantageous to insert between *i* and the pump a reservoir of two or three litres capacity. This reduces the effect of these irregularities very much, and if this reservoir be placed in direct communication with a mercury pressure-gauge, any desired reduction of pressure can, with a little care, be obtained and maintained constant. If the substance under distillation is affected by exposure to the air, any inert gas may easily be introduced instead of air by means of the three-way tap when changing the receiver.

* This has been found a convenient size for general laboratory use, but can of course be modified to suit special circumstances.

XXXVIII.—*Notes on the Condition in which Carbon exists in Steel.*

By Sir Frederick Abel, C.B., F.R.S., and W. H. Deering, F.C.S.

The experiments, the results of which are given in this paper, were made for the Committee on Steel of the Institution of Mechanical Engineers, in the hope of obtaining information on the condition in which carbon exists in steel as it is left by the cold-rolling, and in its hardened, annealed, and intermediate conditions.

The results obtained are considered as preliminary. The earlier series of experiments having showed differences in the behaviour of the hardened steel as compared with the cold-rolled and annealed steel, and in the amount of carbide of iron left by the oxidising solution used, the second series of experiments was devoted to ascertaining the limits of strength of the chromic solution within which approximately the same percentage of carbide of iron would be obtained.

First Series of Experiments.

The steel was used in the form of discs 2·5 inches in diameter, and 0·01 inch thick. Twelve discs were supplied by Mr. Paget of Loughborough, all of which had been cut out of the same strip of metal, the odd-numbered discs (1, 3, 5, &c.) having been cut from one side of the axis of the strip, the even-numbered discs (2, 4, &c.) from the other side. The weight of each disc was about 6·5 grams.

The discs numbered 1, 4, 7 and 10 were the steel as received from cold-rolling. Nos. 2, 5, 8 and 11 were annealed. Nos. 3, 6, 9 and 12 were hardened.

Mr. Paget describes the hardening process as follows. The discs to be hardened were placed between two cast-iron blocks, one being recessed to receive the plates, and the other being quite flat. These blocks were equally heated to a bright red; a disc was then placed between them, and allowed to remain there until thoroughly and equally heated; it was then instantaneously removed, and as quickly as possible caught and pressed between two cast-iron surface-plates.

In the annealing process, the discs were bolted between wrought-iron plates $\frac{3}{8}$ inch thick, and these were then enclosed in a thin sheet-iron box (5 inches square by 2 inches deep). This sheet-iron box was placed in the centre of a cast-iron box (about 15 inches × 6 inches, and about $\frac{3}{4}$ inch thick). The space between the two boxes was filled up with flue-dust (*i.e.*, thoroughly burnt soot taken from the flues of a boiler near to the fire end). The whole apparatus was then raised in an annealing furnace to a bright-red heat, sufficient to scale the cast-

iron box, but not sufficient to fuse it. The fire was then slackened off, banked up with ashes, and the box left in the furnace undisturbed for 24 hours.

From carbon estimations made, the steel discs in contact with the wrought-iron plates appear to lose carbon during this annealing process. Of the annealed discs, Nos. 2 and 11 were those which were in contact with the wrought-iron plates.

Disc No. 6 was used to estimate silicon, which was found to amount to 0·20 per cent.

The total carbon was estimated in one disc of each kind, but an inside disc of the annealed series was examined to compare it with those which had been annealed in immediate contact with the wrought iron. The total carbon was, as usual, estimated by decomposing the metal with cupric chloride solution containing sodium chloride. The filtration was conducted in the combustion-tube itself, so that no loss could arise from transfering the filtering bed and the carbonaceous matter.

The discs in all cases were rubbed bright with fine emery, and cleaned with ether before being used.

The following numbers were obtained for total carbon:—

Disc No. 1 (cold-rolled)	gave	1·108	per cent. of carbon.
„ 3 (hardened)	„	1·128	„ „
„ 5 (annealed, inside disc)	„	0·924	„ „
„ 11 (annealed, outside disc	„	0·860	„ „

An estimation of the so-called uncombined carbon in three of the discs was made by gently heating each disc for three hours with 100 c.c. of hydrochloric acid, sp. gr. 1·10. The annealed and cold-rolled discs dissolved much more rapidly than the hardened disc, the cold-rolled disc furnishing the largest amount of dark-coloured residue. The residues collected on asbestos in the combustion-tubes, washed successively with water, alcohol, ether, and water, were dried, and the carbon estimated by combustion as usual.

No. 7 (cold-rolled)	left	0·096	per cent. carbon.
No. 8 (annealed, inside disc)	„	0·052	„ „
No. 9 (hardened)	„	0·035	„ „

Of the remaining four discs, three were submitted to the action of an oxidising solution—potassium bichromate *plus* sulphuric acid. The solution was made by adding to cold saturated solution of bichromate $\frac{1}{20}$ of its volume of pure concentrated sulphuric acid. The carefully cleaned discs were placed on sieves of platinum gauze and supported in the centre of the chromic solution, 500 c.c. of which was used in

each case, a quantity more than sufficient for the oxidation of the iron contained in a disc. The three discs behaved as follows:—

No. 4 disc, from cold-rolling.—Solution of the metal began at once with rise of temperature, and with a very slight evolution of gas. The liquid was left undisturbed for five days, when there remained upon the sieve a small quantity of black particles, which were attracted by the magnet, and appeared spangly under the microscope.

No. 2 disc, annealed.—Solution of the metal did not commence until after the lapse of five hours, the liquid remaining bright red. Afterwards solution proceeded slowly. At the end of five days a large quantity of black scaly matter remained upon the platinum support; it was attracted by the magnet, and under the microscope had a very spangly appearance.

No. 12 disc, hardened.—The metal was at once attacked with considerable evolution of gas. At the end of five days a small quantity of buff-coloured matter, enclosing a few dark particles, remained upon the sieve. The dark particles were attracted by the magnet, and appeared spangly under the microscope; the light-coloured matter was probably silica. The laboratory temperature, at this time, was about 65° F. in the daytime. In each experiment a small black sediment had collected at the bottom of the vessel, having passed through the sieves. The deposit upon the sieves was washed down into the chromic liquor and allowed to remain in it, at ordinary room temperature for 13 days longer (total duration of treatment, 18 days). The deposits were then collected on asbestos in the tubes in which they were to be burnt; they were washed with water, alcohol, and ether, dried, and burnt in oxygen as usual. The iron was estimated after the combustion.

The following amounts of carbon and iron, calculated upon 100 parts of the discs employed, were obtained from these residues:—

	Carbon.	Iron.
No. 4 (from cold-rolling)	1·039 per cent.	5·87 per cent.
No. 2 (annealed, outside disc) ..	0·830 „	4·74 „
No. 12 (hardened)	0·178 „	0·70 „

Comparing these amounts of carbon with the percentages of total carbon in the corresponding discs, it will be seen that the chromic acid treatment has left very nearly the whole of the carbon from the cold-rolled disc in the form of a carbon-iron compound; and from the annealed still more nearly the whole of the carbon. Thus:—

	Total carbon.	Carbon in residue from chromic treatment.
No. 1 disc (cold-rolled) gave ..	1·108 per cent.	— per cent.
No. 4 „ „ ..	—	1·039 „
No. 11 (annealed, outside disc)	0·860 „	—
No. 2 „ „	—	0·830 „

On the other hand, only about one-sixth of the total carbon of the hardened disc was left in the solid residue by the chromic treatment. In the latter case, too, the ratio of carbon to iron in the residue, was greater than in the residue from the other two discs, thus :—

	Carbon.		Iron.
No. 4 disc (cold-rolled).....	1	:	5·64
No. 2 „ (annealed)	1	:	5·72
No. 12 „ (hardened)	1	:	3·93

It is interesting to observe that in the case of the annealed and cold-rolled discs the ratios correspond very closely; they also correspond closely with the proportions of the elements in an iron carbide having the formula Fe_6C_5.

The last disc was used to see whether the iron carbide would resist the action of a chromic acid solution containing a large excess of sulphuric acid. The disc (No. 10, from cold-rolling) was placed in 500 c.c. of the same chromic solution to which an additional 40 grams sulphuric acid had been added. Solution commenced at once, with evolution of gas; at the end of 24 hours the action was completed, a quantity of heavy black powder remaining. This was left in the solvent for nine days, when it gave on analysis 0·84 of carbon and 1·104 of iron per 100 of disc.

With this large excess of acid the carbide broke down; but while the greater part of the iron was dissolved, most of the carbon remained in a solid insoluble form; probably the residue consisted of iron carbide and carbohydrate.

It would have been very desirable to have treated these residues with hydrochloric acid, to have ascertained how much of the carbon would have been converted into hydrocarbons, but the material was used up, and the preparation and more complete examination of the carbide of iron was reserved for further experiments.

Before giving the result of further experiments, it will be convenient here to give some account of previous work on the relation of iron to carbon.

Karsten gives for the composition of iron completely saturated with carbon at the melting point of the resulting compound, numbers agreeing with Fe_4C (atomic weight iron probably 27 and C 6). This

is from the analysis of a spiegeleisen, but as Percy has pointed out, Karsten did not look for manganese.

Faraday and Stodart prepared a dark-grey fusible carbide of iron by fusing finely-divided iron or steel with charcoal once or more. An analysis by them is given in *Gmelin's Handbook*, which probably refers to this preparation. They found 94·36 per cent. Fe, and 5·64 per cent. C; one constituent is probably estimated by difference, and no mention is made (in *Gmelin*) of the absence or presence of manganese. Recalculating the formula for Fe = 56, C = 12, the numbers would be intermediate between Fe_4C and Fe_3C.

Percy intensely heated pure sesquioxide of iron with excess of carbon, and obtained buttons of, in the cold, highly graphitic iron. One preparation contained 95·80 per cent. iron; a second, 95·66 per cent. iron, and 4·56 per cent. graphite; a third, 95·85 per cent. iron; a fourth, 95·13 per cent. iron, and 4·63 per cent. graphite. From the iron estimations, 4·15 per cent. would be the lowest, and 4·87 per cent. the highest amount of carbon taken up by the melted iron.

Karsten also describes a carbide of iron, FeC_3, left by the action of dilute acids on slowly cooled bar-iron or steel, the action not being allowed to go on too long. The residue is described as a graphite-like but magnetic mass, which if burnt after washing and drying, leaves from 82—94 per cent. ferric oxide, and is probably therefore FeC_3 (*Gmelin's Handbook*). The substance described is obviously very indefinite in composition, and Karsten himself at a later date admitted that there was no satisfactory proof of the existence of such a carbide.

Berthier's preparation of a carbide FeC from cast steel by means of bromine or iodine was unsatisfactory, there being no definite stopping point to the action. Caron was unable to prepare Berthier's definite carbide, and regards it as probably only a mixture of carbon and metal, in which the latter was mechanically protected by the carbon from solvent action.

Faraday and Stodart state that hardened steel immersed in dilute sulphuric acid becomes covered with a small quantity of black metallic powder; unhardened steel, in the same time, with eight times as much of a grey powder, which is soft, coherent, and may be cut with a knife, and appears to consist of carbide of iron.

Karsten, too, had observed qualitative differences between the behaviour of dilute acids on hardened and unhardened steel.

The above statements, and numerous published analyses of cast iron, &c., are about the sum of definite statement on the combination of iron and carbon. As regards the amount of carbon required to saturate carburetted iron in a state of fusion, Percy's experiments give 4·87 per cent. carbon as a maximum.

It is difficult to draw conclusions from the analyses of cast iron, on

account of the general presence of manganese in the specular, or white irons, or on account of the presence of silicon in large quantity, and on account of uncertainty whether the fused carburetted iron has been supplied to saturation with carbon.

Instead of saturating iron with carbon at a temperature above the fusing point of the resulting carbide, and finding the once liquid (and, probably, chemically combined) carbon from the estimation of total carbon in the solidified compound, we have endeavoured to dissolve away the excess of metallic iron from a steel containing about 1 per cent. carbon.

At this amount of carbon the iron is unsaturated, and the material is free from uncombined carbon. The use of a solution of chromic and sulphuric acids has over the dilute sulphuric or hydrochloric acid used by earlier experimenters the advantage that the formation of hydrogen is to a very great extent prevented, and a visible stopping point in the action afforded by the inability of the carbide of iron to effect further reduction of chromic acid.

Second Series of Experiments.

The steel used was in the form of a thin sheet, weighing 175 grams, and about 0·008 inch in thickness. It had been melted from cemented blister steel, the ingot having been subsequently cold-rolled and cross cold-rolled, and annealed several times between the various rollings.

A part of the sheet was analysed; it contained:—Carbon, 1·144 per cent.; silicon, 0·166 per cent.; manganese, 0·104 per cent. Two-thirds of the steel was used up in experiments, then another estimation of total carbon was made; 1·108 per cent. carbon was found. The former number (1·144 per cent.) was taken for purposes of calculation. It was desired to learn more about the magnetic carbon-iron compound obtained in the former experiments, and more especially to obtain information on these three points:—1st, whether its composition is independent, within rather wide limits, of the strength of the chromic solution employed; 2nd, whether, within those limits, a constant quantity of carbide is obtained per 100 of steel; and 3rd, how much of the carbon of this carbide, upon treatment with hot hydrochloric acid, would remain unconverted into hydrocarbons.

The weight of steel submitted in one vessel to the action of the chromic solution was about 7—7·5 grams. Before using them, the pieces were rubbed bright with emery, and cleaned with ether.

The chromic acid solutions used may be conveniently referred to that used for preparation 2. This was prepared by adding to a cold (67—68° F.) saturated solution of potassium bichromate, and containing 99 grams of the salt per 1000 c.c. solution, pure concentrated sulphuric

acid in the proportion of 0·9 gram of acid to 1 gram of the bichromate. The equation $Fe_2 + K_2Cr_2O_7 + 8H_2SO_4 = Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 2KHSO_4 + 7H_2O$ requires 0·84867 gram of sulphuric acid to 1 gram of the bichromate, and 1000 c.c. of the solution thus prepared would dissolve 9·226 grams of iron. The strength of the solutions was also checked by estimation of the available oxygen. The amount of solution employed was always considerably in excess of the amount required to dissolve the steel used.

The solution used in obtaining preparation 1 was a little weaker, being 0·8 the strength of the solution for preparation 2.

Preparation 3 was produced with a much weaker chromic solution; the strength aimed at was 0·5 that of preparation 2; its actual strength was 0·44.

For preparation 4 a hot solution of bichromate was mixed with the requisite quantity of sulphuric acid (1 gram bichromate to 0·9 gram sulphuric acid), and the strength aimed at was double that of preparation 2. Two different quantities of the liquid were prepared, but in both the strength exceeded that of the solution of preparation 2 only by about one-half (being 1·44 of its strength in chromic acid in one case, and 1·65 in the other), a little chromic acid having in both cases crystallised out, together with potassium bisulphate, on cooling.

The mode of treatment of the steel by the chromic solutions was in all instances alike. The solvent was contained in a beaker, and the weighed piece of steel was supported at about the centre of the liquid upon a sieve of platinum wire gauze. The steel, though thoroughly cleaned, would frequently remain unattacked in the liquid, even for days, if simply immersed and left at rest; but the action was started at once by moistening the steel with the chromic solution, and exposing it to the air in that state for a minute or two before immersion. The small platinum sieves were placed in funnels covered by dial-glasses, and supported in the liquid by glass cylinders. The heavy solution of ferric sulphate passed down through the funnel as produced, and thus a continuous circulation of the solvent was promoted. The experiments were made at ordinary laboratory temperatures.

Preparation 1.—Four pieces of the steel (from 7—7·5 grams each) were exposed in separate vessels to the action of the solvent of the strength described; 1000 c.c. of the solution was used to each piece of steel. Examined at the end of two days, there only remained small quantities of a grey-black powder upon the sieves; this was washed off into the chromic liquor and, together with the powder which had collected at the bottom of the vessel, was allowed to remain from 8—14 days in the solution, the time varying with the date at which the several experiments had been commenced. In each case there was a considerable excess of chromic acid in the solution. The four deposits

were then transferred to one vessel; 500 c.c. of the fresh chromic solution were placed upon the combined product, which was allowed to remain in the solvent for four days at the ordinary temperature. During this time no reduction of chromic acid took place. The product was a heavy grey-black powder, strongly attracted by the magnet; it was washed by decantation, first with water several times, then with alcohol, finally with ether, and was then dried in a vacuum over sulphuric acid, until it ceased to lose appreciably in weight. The liquids used in washing were filtered, and the iron in the quite small amount of material on the filter estimated, calculated into carbide by means of the numbers obtained by the analysis of the bulk of the product, and the number added to the directly weighed carbide.

The amount of dry residue, or carbide, thus obtained per 100 parts of steel was 13·25.

The first two analyses were made by the copper chloride process, the iron being estimated in the filtrate, after the copper had been converted into sulphate and precipitated by an electric current. But the substance was attacked with difficulty by the copper chloride, there being no action at the ordinary temperature even after the lapse of 24 hours. This affords additional proof that metallic iron had been completely removed by the chromic treatment. The substance and copper chloride had therefore to be heated, probably with some slight loss of carbon, by its conversion into hydrocarbons. The carbonaceous residue, too, was left in so very finely divided a condition as to make filtration a matter of some difficulty.

For these reasons, after the first two analyses, the carbides were analysed by direct combustion in a porcelain boat in oxygen, the gases being passed over a short length of oxide of copper in the usual way. The iron was then estimated in the residual iron oxide in the boat.

The water produced in the direct combustions was also weighed. The amount of water gives an indication of the thoroughness of the drying of the material, and by the great increase in the percentage of water obtained in preparation 4, shows that in that preparation decomposition of the iron carbide had taken place, with formation of carbohydrate. The long contact of the carbides with excess of chromic acid solution would prevent their containing absorbed hydrogen.

Although great care was exercised, the water estimations are probably, from the nature of the experiments, slightly too high.

The first two analyses of preparation 1, made by the copper chloride process, gave 6·83 and 6·69 per cent. carbon. The iron (in these two analyses estimated after precipitation of the copper by electricity) amounted to 91·29 and 92·16 per cent.

By direct combustion, the following were the amounts obtained per 100 of carbide:—

Carbon	7·31
Iron	90·42
Water	2·37

The carbide contained no silica.

In order to ascertain what proportion of the carbon this product would leave unconverted into hydrocarbons by treatment with hydrochloric acid, from 0·5 to 1 gram of the carbide was heated upon a water-bath with excess of the acid (of sp. gr. 1·10): the undissolved matter was collected on asbestos, washed successively with cold water, cold alcohol, and warm ether, then heated in a current of hydrogen, and afterwards the carbon was estimated by combustion, &c., as usual, in oxygen.

In two experiments the carbon unconverted into hydrocarbons amounted to 1·410 per 100 of the carbide, or 20·87 per 100 of carbon in the carbide, and 1·238 per 100 of the carbide, or 16·93 per 100 of carbon in the carbide.

Preparation 2.—The chromic solution used has been already described as that of preparation 2. Two pieces of steel, each weighing about 7·5 grams, were each treated with 1250 c.c. of the chromic solution, and the treatment carried on for four days. The two products, of the same nature as those constituting preparation 1, were then transferred to one vessel, and left for two more days in contact with 250 c.c. of fresh chromic solution, which appeared unaltered at the end of that time.

The amount of carbide thus obtained per 100 of steel was 14·16.

The dried product gave by direct combustion the following percentage numbers:—

Carbon	7·21
Iron	90·64
Water	2·27

The carbon remaining unconverted into hydrocarbons, by treatment of this product with hydrochloric acid, amounted to 1·269 per 100 of the carbide, or 17·60 per 100 of carbon in the carbide.

Preparation 3.—Two pieces of steel, each about 7·5 grams in weight, were treated for five days in separate vessels each with 2000 c.c. of the comparatively weak chromic solution already described as that of preparation 3. The united products were afterwards left for five days in 500 c.c. of fresh chromic solution, which did not appear at all reduced.

The amount of carbide obtained per 100 parts of steel was 15·34.

Direct combustions of the carbide gave the following percentage numbers:—

Carbon	6·84	6·84	—
Iron	91·53	91·50	91·50
Water	1·63	—	—

The carbon unconverted into hydrocarbons by treatment of the carbide with hydrochloric acid amounted to 0·836 per 100 of the carbide, or 12·22 per 100 of carbon in the carbide.

Preparation 4.—14·7 grams of the steel were treated with the chromic solutions described as those of preparation 4. The steel was treated for three days with 1900 c.c. of the chromic solution of 1·44 times the strength of the solution used for preparation 2. The product obtained was afterwards left in contact with 350 c.c. of the strongest solution (1·65 times the strength of the solution of preparation 2), which appeared at the end of that time but very slightly reduced.

The amount of product obtained from 100 parts of steel was only 4·66.

A direct combustion showed that it had the following percentage composition:—

Carbon	11·77
Iron.....	80·57
Water.....	5·57

The deficiency of about 2 per cent. from 100 is probably owing to the presence of oxygen in the material, in excess of that required to form water. This product, although like the others attracted by the magnet, was darker in colour, and was evidently a mixture of iron-carbide, and oxidised carbohydrate resulting from the decomposition of the iron carbide.

There was not sufficient material for a second analysis, nor for treatment with hydrochloric acid.

The amount of carbon unconverted into hydrocarbons, by treatment of the original steel with hydrochloric acid, was determined and found to be 0·039 per 100 of steel, or 3·41 per 100 of carbon in the steel.

The results obtained in these four preparations are given in tabular form:—

	Preparation 1.	Preparation 2.	Preparation 3.	Preparation 4.
Carbide obtained per 100 of steel.	13·25	14·16	15·34	4·66 or 4·00 per cent. Fe_3C.†
Composition per 100 of carbide :—				
Carbon	7·31	7·21	6·84	11·77
Iron.....	90·42	90·64	91·50	80·57
Water.....	2·37	2·27	1·63	5·57
Atomic ratio	$Fe_{2\cdot65}C_1$	$Fe_{2\cdot694}C_1$	$Fe_{2\cdot867}C_1$	—
Parts of carbon obtained in form of carbide per 100 of steel.*	0·969	1·021	1·049	0·266†
Parts of carbon unconverted into hydrocarbons by treatment of carbide with HCl :—				
Per 100 of carbide..	1·410 1·238	1·269	0·836	—
Per 100 of carbon in the carbide.	20·87 16·93	17·60	12·22	—

An examination of the foregoing results suggests the following observations :—

1. The two chromic solutions used for preparations 1 and 2 (made from cold saturated, and nearly saturated potassium bichromate) gave very similar results, both in respect of the percentage of product obtained from the steel, and of the percentage composition of the product. The third, a much weaker solution, furnished results which, allowance being made for the small quantities of substance dealt with, and inherent analytical difficulties, must be regarded as closely resembling those obtained with the other two solutions.

The time during which the steel was treated with the chromic solutions might be advantageously greatly shortened. The treatment was protracted to ensure removal of excess of metallic iron, but it may also have caused some formation of carbohydrate.

2. The results obtained with the strongest chromic solution (preparation 4) indicate that the limit of concentration of the oxidising solution which the separated carbide is capable of resisting has here been exceeded. Not only has there been in this case a very considerable loss of carbon as hydrocarbons (or possibly also as a soluble

* Had no loss of carbon (from formation of hydrocarbons, or otherwise) attended the chromic treatment, the amount of carbon obtained as carbide should have been 1·144 per cent., that being the total amount of carbon in this steel.

† In this case calculated from the iron, taking the composition of the actual carbide present, as Fe_3C.

product of oxidation), but the iron in the separated carbide has also been to a considerable extent attacked, and only a relatively small proportion of the carbide remains, together with separated carbon, the latter partly in a hydrated form, and possibly also in some partially oxidised insoluble form.

3. The small amounts of water obtained on combustion of preparations 1, 2, and 3, may indicate that, in these also, small quantities of carbohydrate are present with the iron carbide. This may result from the action of the chromic solutions on the carbide first separated, and may account for the not very definite, though on the whole uniform, atomic ratio of iron to carbon in the products of preparations 1, 2, and 3.

4. If the carbon unconverted into hydrocarbons by treatment of the products with hydrochloric acid be deducted from the percentages of total carbon in the products of preparations 1, 2, and 3, the results exhibit a uniformity which, if accidental, is somewhat remarkable. Thus:—

	Preparation 1.	Preparation 2.	Preparation 3.
Per cent. of total carbon...	7·31	7·21	6·84
Less carbon unconverted into hydrocarbons	1·38	1·27	0·84
There remain of carbon per cent.	5·93	5·94	6·00

The atomic ratio of this residual percentage of carbon to iron is as 1 to 3·270 of iron.

Although the hydrogen yielded by an iron carbide Fe_3C, with hydrochloric acid, viz., H_6 to C_1, would, theoretically, more than suffice for the conversion of the carbon even into paraffins, it is yet very possible that some hydration of carbon might take place as well as the predominating hydrogenisation.

To obtain information as to the relative amount of combined carbon hydrogenised and hydrated, an experiment was made with commercial ferromanganese, containing nearly as much carbon as the carbides from steel just described. The ferromanganese contained total carbon, 6·50 per cent.; manganese, 83·90 per cent.; iron, 8·10 per cent.; silicon, 0·45 per cent. It is interesting to observe that it has the composition of a substituted trimanganese monocarbide,

$$(\tfrac{1}{1}\tfrac{1}{2}\mathrm{Mn}.\tfrac{1}{1}\tfrac{}{2}\mathrm{Fe})_3C_1.$$

The ferromanganese in powder was heated with HCl, and the oil and carbonaceous matter were treated like the steel preparations, *i.e.*,

filtered, treated with alcohol, then with ether, then dried, and the residual carbon estimated by combustion as usual. Obtained of carbon unconverted into hydrocarbons, 0·975 per 100 ferromanganese, or 15 per 100 parts of carbon. This proportion of unhydrogenised carbon is very nearly the average of the amounts obtained by similar treatment of the first three preparations of steel carbide.

The carbonaceous residue of the action of hydrochloric acid on ferromanganese was digested with caustic potash (sp. gr. 1·1), but in this case, as in others, a small quantity of silica only, and not a soluble (in potash) carbon-hydrate, was removed. It is improbable, however, that this carbonaceous residue was graphite, which it did not resemble.

5. The carbon separated in the solid form as carbide and carbohydrate more nearly approaches the total amount (1·144 per cent.) of carbon contained in the steel, in the case of No. 3, when the weakest chromic solution was employed, a result which was anticipated.

6. On the whole these results, which are in all respects more complete than those obtained in the first preliminary series of experiments, afford foundation for the belief that the material separated from cold-rolled steel by the action of chromic and sulphuric acid solutions below a certain strength, contains an iron carbide approximating to the formula Fe_3C_1, or a multiple of that formula. The numbers required by Fe_3C_1 are intermediate between those furnished by the original percentage composition of preparations 1, 2, and 3, and these after deduction of the unhydrogenised carbon.

The protracted treatment with the chromic acid solutions in the second series of experiments makes it surprising that in the first series much less iron proportionally to the carbon should have been obtained. Had there been material for estimation of so-called uncombined carbon and water, it might have been found that much of the carbon in the two carbide preparations of the first preliminary experiments was not in combination with the iron.

The results of these experiments with cold-rolled steel of a particular composition appear to confirm the correctness of the view that the carbon in cold-rolled steel exists, not simply diffused mechanically through the mass of steel, but in the form of an iron carbide, a definite product capable of resisting the oxidising effect of an agent which exerts a rapid solvent action upon the iron through which the carbide is distributed.

Whether this carbide varies in composition in different descriptions of steel which are in the same condition of preparation (*i.e.*, cold-rolled or annealed) must be a subject for further experiments. The preliminary experiments already described with small specimens

of cold-rolled, annealed, and hardened steel appear to warrant the belief that the condition of the carbide in the metal is so affected by hardening as very greatly to diminish its power to resist the decomposing effect of such an oxidising agent as chromic acid solution.

It is hoped that opportunity may be found to continue these experiments with unfused cementation steel, and with other ingot steels, in the same and in different conditions of temper, using the weakest chromic solution, which gave the most favourable results; also to examine the behaviour of carbon and manganese, the statements about which are not very precise.

XXXIX.—*On the Spectrum of Beryllium, with Observations relative to the Position of that Metal among the Elements.*

By W. N. Hartley, Royal College of Science, Dublin.

The element beryllium is one which presents unusual difficulties in its preparation in a pure state, owing to its tendency to combine with silicon and to take up iron and aluminium. The specimen used by Messrs. Nilson and Pettersson for the determination of its specific heat, notwithstanding all the skill and care bestowed upon its preparation, nevertheless contained from 5·59 to 13 per cent. of impurities (*Proc. Roy. Soc.*, 1880, **31**, 37; and *Chem. News*, **42**, 297). The metal was not homogeneous, being partly crystallised and partly in the form of fused globules. It is therefore still questionable whether beryllium is a triad element with an atomic weight of 13·8, an oxide of the formula Be_2O_3 and a specific heat of 0·4079 to 0·4083 (Nilson and Pettersson), or a dyad element with atomic weight 9·2, an oxide BeO, and specific heat 0·642, as calculated from experimental evidence by Dr. Emerson Reynolds. In some hope of throwing light upon this difficult subject, I have long been anxious to examine the spectrum of beryllium, because, although there are only two rays which have been observed and measured in the visible spectrum (wave-lengths 4572 and 4488, Kirchoff and Thalén), yet, as I have elsewhere pointed out (*Chem. Soc. J.*, **41**, 84), the spectra of the elements generally present their most characteristic features in the ultra-violet region. Moreover, when two octaves of the spectrum are under observation there is more likelihood of discovering analogies between spectra than when only half that compass of vibrations is viewed. Investigators of spectra have already rendered good service in determining the atomic

weight of the metal gallium, for M. Lecoq de Boisbaudran calculated its value to 69·86 from a comparison of the spectrum of this element with those of aluminium and indium on the one hand, and of potassium, rubidium, and cæsium on the other. The number determined by weighings was 69·87 (*Wurtz' Dictionnaire de Chimie*, New Supplement, p. 859).

The considerations which guided me in this research were the following:—If beryllium is a triad body with an oxide Be_2O_3, it may be expected to exhibit a spectrum showing considerable analogies with those of aluminium and indium, that is to say, the principal lines will consist of three pairs apparently harmonically related, the interval between the individuals of each pair increasing with increased refrangibility of the rays, and the interval between each pair of lines will contain an isolated ray, but as the atomic weight of beryllium is less than that of aluminium, the interval between the members of each pair of lines will be shorter. Pairs of lines somewhat similarly related are characteristic of the groups calcium, strontium, and barium, but the single lines are absent, and the intervals are different. The question, however, whether beryllium is a dyad, and the first member of the series magnesium, zinc, cadmium, is complicated, since it would probably present a spectrum of a different character to the succeeding homologues, in accordance with the following equation, which follows from the periodic law, and holds good for the chemical properties of compounds:—

$$Li : Mg = Be : Al = B : Si.$$

The relation of the spectrum of lithium to that of magnesium is obscure, that of boron to silicon is less so, consequently we might expect that the relation of the beryllium spectrum to that of aluminium would not be well defined. There is a periodic variation in the spectra of the elements as well as in their atomic weights and chemical properties, and we cannot put the periodic law out of mind in considering the position of beryllium.

The material employed for producing the spark spectrum of beryllium was a saturated solution of the chloride prepared from pure oxide kindly presented to me by Dr. J. Emerson Reynolds. The salt so obtained was remarkably pure, for the photograph of its spectrum showed no lines of any elements known to me except two very faint lines of calcium which were present in the hydrochloric acid. Both prism and diffraction spectra were photographed, the latter being produced by a speculum ruled with Mr. Rutherford's engine, and containing 17,460 lines to the inch. The lenses of the camera and collimator tube were 36 inches in focal length. Of the two weak lines in the visible spectrum one only was photographed, and that was too faint to be measured.

The Spectrum of Beryllium.

Number of line.	Wave-length.	Description.
(3)	3320·5	Strong, sharp.
(4)	3130·2	Very strong, extended.
(5)	2649·4	Strong, sharp.
(6)	2493·2	Strong, sharp.
(7)	2477·7	Strong, sharp.

In examining solutions, some of the characteristics of the spectra taken with metallic electrodes are modified; thus of the short lines some disappear and others become long lines. On taking dilute solutions for examination, the most persistent line of beryllium is No. 4, and the order in which the lines disappear is No. 3, 5, 6, 7.

The line 3130·2 is given in M. Cornu's map of the solar spectrum as double, the measurements being 3130 and 3130·4, and no other lines appear. This measurement doubtless was taken from an arc spectrum. The line in my photographs is particularly sharp but somewhat broad. As I have no difficulty in easily distinguishing between two lines separated by 0·4 of a tenth-meter, and as faint impressions of the line failed to show any indication of its being double even under a magnifying power of 25 diameters, I conclude that the spark yields only one line here.

I have mapped the beryllium lines according to their wave-lengths, and in order to make the spectrum comparable with those described in my paper on homologous spectra, I have added a map on the scale of wave-frequencies.

If, as Nilson and Pettersson suggest, the position of beryllium is at the head of a series of triad rare earth-metals, the elements scandium (at. wt. = 44) and yttrium (at. wt. = 89) must be members of the same series (*Kongl. Svenska Akademiens Handlingar*, **12**, 4). If this be the case, the spectra of the three elements must have certain characters in common, for the series of which aluminium and indium are the first and third terms yield strictly homologous spectra. Indeed scandium must occupy the place next to beryllium if the atomic weight of the latter is 13·8, and the similarity between the spectra of the two elements must be exceedingly close. As a matter of fact, no two spectra could be more dissimilar than those of beryllium and scandium. According to Thalén, scandium yields no fewer than 103 visible lines (*Compt. rend.*, **91**, 45), and yttrium yields 90. Both spectra contain highly characteristic groups of lines in the orange and yellow, the lines or bands degrading towards the red. Certainly beryllium can find no place in the same series with two such elements whose atomic weights being 44 and 89 differ from 13·8 by no very great quantities. The multitude of lines is in no way consistent with

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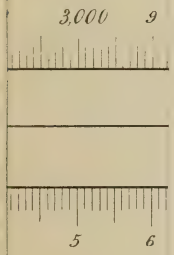
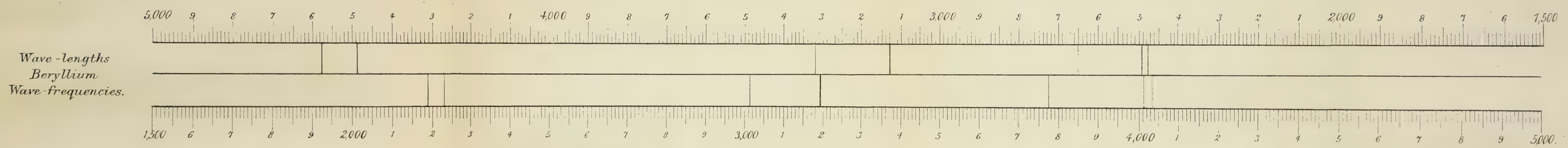


THE SPECTRUM OF BERYLLIUM.



Harrison & Sons, Lith. St. Martins Lane W.C.

such an increase in the atomic weights. Having compared a great variety of spectra with that of beryllium, I am justified in making the following remarks:—

The spectrum of beryllium exhibits no marked analogy with the calcium, the magnesium, or the aluminium spectra, all of which are members of well-defined homologous series. There is nothing similar to the boron, the silicon, or carbon spectra, nor to those of scandium, yttrium, or cerium. The spectrum of lithium is the one most allied to that of beryllium in the number, relative position, and intensity of the lines. The character of the lines of greatest intensity in the beryllium spectrum is more like that of the pairs of lines in the spectrum of calcium with wave-lengths 3933—3967·5 and 3705·5—3736·5. In fact the similarity to the line 3705·5 is so great that the two when juxtaposed on one plate may be mistaken if their positions be not taken into account. Lines of similar elements have very distinctive features. Individual lines of the calcium, strontium, and barium group are quite different from those of the magnesium, zinc, cadmium series, and they could not be mistaken. The lines of cerium and didymium again are quite dissimilar in character; instead of being broad they are exceedingly fine.

I am therefore led to the conclusion that beryllium is the first member of a dyad series of elements, of which in all probability calcium, strontium, and barium are homologues.

XL.—*On a New Oxide of Tellurium.*

By Edward Divers, M.D., Principal, and M. Shimosé, Student of the Imperial Japanese College of Engineering.

By heating in a vacuum the compound of sulphur trioxide and tellurium until it decomposes, we have obtained sulphur dioxide and a new oxide of tellurium. This oxide is in the solid state, and if sufficiently heated, suffers decomposition into tellurium dioxide and elemental tellurium, the latter volatilising before the former. Decomposition of the sulphoxide begins—according to our observations, which differ from R. Weber's—at about 180° C., but is not quite complete even at about 230°, above which temperature we have feared to pass, lest we might cause some of the new oxide to decompose.

The operation was carried on in a tube-retort, immersed in a paraffin-bath, and connected with a Sprengel pump. In this vessel

the required sulphoxide had itself been prepared and purified, ready for the experiment, and out of contact with the air.

The solid sulphoxide softens by the heat to a pasty mass before decomposition sets in, and when this happens, intumesces very much in giving off the resulting sulphur dioxide. At the same time its own lustrous brown colour gives place to the black colour, also lustrous, of the new oxide. The oxide now exhibits a marked resemblance to charred cork.

It is not yet quite pure. Even prolonged heating in a vacuum failed to yield it altogether free from a sulphur-compound, which can hardly be other than unchanged sulphoxide of tellurium. We have, therefore, with the view of purifying it, rubbed the vesicular mass to powder, and washed it with water holding in solution a small quantity of sodium carbonate. This treatment effectually removes oxide (or oxides) of sulphur, together with any tellurous acid that may have resulted from the decomposition of the sulphoxide, this acid being readily soluble in sodium carbonate. Washing with hot water to remove soda, and with alcohol to remove water, and then rapid drying in the water-oven, complete the preparation of the new compound.

As thus prepared, however, it may still contain free tellurium resulting from the action of water on the sulphoxide, insignificant indeed in quantity if the heating in the vacuum has been strong and protracted, or perhaps entirely absent. For, as we shall describe further on, the new oxide appears to be one of the products of the decomposition of the sulphoxide by water, and is undoubtedly the first tellurium-product of the reaction, the free tellurium being only a secondary product. The sulphoxide being here present in very small quantity only, and spread through a mass of the new oxide, is probably in the condition most favourable to the permanence of the products of its primary decomposition. Be this, however, as it may, experience and practice have enabled us so to improve our working as at last to prepare the oxide unmixed with any quantity of free tellurium sufficient to betray its presence on analysis, whereas at an earlier stage of our work, we obtained evidence of the presence of small quantities of tellurium diminishing in successive preparations.

The new oxide seems also to be obtained in small quantity by the action of water on the sulphoxide. This action, as Weber has pointed out,* results in the production of tellurium, tellurous oxide, and sulphurous acid. But besides these substances, there are also formed sulphuric acid and, apparently, the oxide of tellurium here described. For we find the black matter precipitated by this action, not only to

* Abstracts in this Journal, **42**, 804, and in the *Berichte*, **15**, 1336, of the paper in *J. pr. Chem.*, **24**, 218.

differ somewhat in aspect from tellurium reduced by sulphurous acid, in being brownish rather than bluish-black, but also to yield some tellurium dichloride when acted upon by dry hydrochloric acid. The greater part of the precipitate is undoubtedly free tellurium, and this part remains unaffected by the hydrochloric acid. If the oxide here present were the dioxide, it too would, in contact with the free tellurium, give the dichloride with hydrochloric acid, the tetrachloride being an intermediate product. But the fact of the previous washing with sodium carbonate should preclude the supposition of its presence.

The well-known purple-red solution of tellurium in sulphuric acid, when poured gradually into a very large volume of water, also yields the new oxide, apparently together with the other products obtained from the sulphoxide. But tellurium dichloride, decomposed by water, gives no monoxide even where the water used contains alkali, the sole products being hydrochloric acid, tellurous acid, and free tellurium.

The new oxide of tellurium is quite stable in dry air at common temperatures. It is black in colour with a slight brown shade, and shows, when pressed with a hard body, a graphitic lustre quite distinct from that of powdered tellurium itself, which, when the tellurium is pressed, is light-grey and much brighter.

Its composition may be expressed by the name and formula *Tellurium monoxide*, TeO, but its constitution is probably more complex than such a name and formula indicate. Its composition has been ascertained by oxidising it with bromine in hydrochloric acid water, precipitating the tellurium with sulphurous acid, washing the precipitate on a tared filter, and weighing. Using 0·3179 gram of one preparation, and 0·3378 gram of another, we obtained quantities of tellurium corresponding to 90·0 and 88·8 per cent. respectively. Taking Te as 128 and calculating for TeO, the tellurium comes out 88·9 per cent.

Heated strongly in a vacuum, tellurium monoxide decomposes, as already stated, into tellurium dioxide and tellurium. Heated in the air, it slowly oxidises to dioxide. In the moist state, it slowly cakes together, apparently by formation of dioxide; but whether by oxidation, or by a decomposition with water in which tellurium is liberated, or in both these ways, we have not yet determined.

Potassium hydroxide in cold solution acts but slightly upon it; but when boiled with it gradually decomposes it, leaving elemental tellurium undissolved. It is much more unstable in presence of acids. Even cold dilute solutions of hydrochloric or sulphuric acid act markedly upon it, while hot fuming hydrochloric acid at once decomposes it into tellurium and its dioxide, the latter, of course, dissolving.

It is readily oxidised by nitric acid and by acid oxidising solutions, less easily by neutral or alkaline solutions. Potassium permanganate is reduced by it to manganate. It is but little acted upon by sulphur dioxide solution in absence of acids, but is slowly reduced by it to the elemental state.

Liquid sulphur trioxide appears to be without any action upon tellurium monoxide, even when boiled upon it. The monoxide becomes, indeed, slightly reddened, but remains otherwise unchanged, and when heated, does not exhibit the least intumescence, as it would do if converted into sulphoxide. The slight reddening observed may with certainty be attributed to the action of a trace of sulphuric acid, partly in the sulphur trioxide, partly formed by hygroscopic moisture in the tellurium monoxide. Sulphuric acid is immediately and strongly coloured red by the monoxide, which dissolves completely in it, but rapidly deposits a considerable quantity of crystalline tellurous sulphate—

$$2TeO + 3SO_4H_2 = Te(O_4S)_2 + SO_3Te + 3OH_2.$$

Hydrochloric acid gas is absorbed by it, but without much apparent change until a gentle heat is applied, when it partly melts to a brownish-black liquid, and then sublimes as a dark-greenish powdery solid, which is decomposed by water into hydrochloric acid, tellurous acid, and tellurium, and is therefore the already known dichloride of tellurium.

No compound of tellurium monoxide has been obtained by us, and we are unable to assign to it either acid or basic properties. Analogy would make it basic, since the dioxide can act as a feeble base. The monoxide is, however, very probably of complex constitution, more complex than the dioxide can be.

The existence of this new substance only in the solid and amorphous state, and its inability to form compounds, unless we regard the sulphoxide as one, may, perhaps, suggest to others, as such facts did at first to us, doubts of its individuality. We will, therefore, state the results of an examination we made for comparison of the properties of a mixture of free tellurium with an equal weight of tellurium oxidised to dioxide. The tellurium used was in the reguline state rubbed to fine powder. Precipitated tellurium, not easily obtained so pure, was found to be scarcely more sensitive to reagents than the monoxide obtained as above.

This mixture is whitish-grey, and remains so after it has been heated, like the monoxide, to 230° in a vacuum. It is at once resolved by a solution of potassium hydroxide into its ingredients. In cold hydrochloric acid gas it becomes wet, in consequence of formation of the liquid tetrachloride from the dioxide. When heated,

the mixture of tetrachloride and free tellurium behaves, of course, like the monoxide, in yielding the dichloride.

The behaviour of the mixture in liquid sulphur trioxide is strikingly unlike that of the monoxide. It assumes a light-pink colour, and is changed into a mixture of unaltered tellurium dioxide and tellurium sulphoxide, and when the mixture is heated, causes it to swell up enormously. It is, perhaps, necessary to mention here that tellurium dioxide and sulphur trioxide do not combine together. Lastly, in sulphuric acid, the mixture becomes mechanically separated into its ingredients, the dioxide rendering it milky, while the free tellurium is deposited, and dissolves very slowly and slightly, forming a pink colour.

XLI.—*On Tellurium Sulphoxide.*

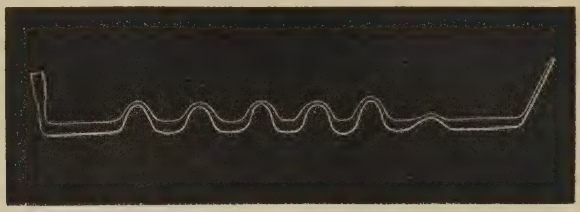
By Edward Divers and M. Shimosé.

In connection with a reaction which we had observed between sulphuric acid and tellurium compounds, we made experiments, some time ago, upon the action of sulphur trioxide upon tellurium. These resulted in the discovery of the sulphoxide of tellurium, of which, at that date, no account had then reached us. But, soon afterwards, we found in the number of the *Berichte* for June, and that of the Journal of this Society for August, abstracts of Rudolph Weber's paper announcing the prior discovery of this substance. On reading these accounts, however, we noticed that our results were not quite in accordance with his, and we therefore proceeded to complete our own experiments.

The Tellurium used.—We obtained tellurium free from the mud of the lead chambers of the Imperial Japanese Sulphuric Acid Works in Osaka. The greater part of the tellurium existed in the weak acid supernatant liquor of the mud. This mud had been exposed to the air for a long time, and the tellurium had become oxidised and dissolved during the exposure. From this liquor the tellurium, mixed with a little selenium, was precipitated by hydrogen sulphide. The washed precipitate was dissolved in nitrohydrochloric acid, and the solution precipitated by sulphur dioxide. The washed precipitate was dissolved in melting potassium cyanide, and the product, after cooling, treated with water. After leaving the mixture at rest, the clear solution was decanted from insoluble matters, and precipitated by a

current of air. The precipitate was washed and dried, and distilled in a hard glass tube in a current of carefully purified hydrogen.

The Sulphur Trioxide used.—This was prepared, and rectified, and combined with the tellurium in a piece of glass apparatus, consisting of a piece of combustion-tube drawn out as shown in the figure.



The tellurium, finely powdered, and dried in a water-oven was introduced, in weighed quantity, into the seventh receptable, through the drawn-out end of the tube. The tellurium did not adhere to the sides of the tube. Dried air having been passed through the apparatus for a considerable time, both before and after the introduction of the tellurium, the drawn-out end was sealed. Through the other end a considerable charge of sulphuric acid and phosphorus pentoxide was then introduced into the first receptacle, and the funnel-like end sealed off in the lamp. Ice having been applied to the second receptacle, the mixture in the first was gently heated until enough sulphur trioxide had distilled into the second. The first receptacle was then sealed off. The sulphur trioxide was next successively distilled into the third, fourth, fifth, and sixth receptacles. Only in the second was there any sensible residue after very gentle heating. The other receptacles having been sealed off, one after the other, there remained only two in connection, one holding the sulphur trioxide, the other the tellurium. The sulphur trioxide thus prepared was a mobile liquid, crystallising in transparent prisms, and having for some time, at least, a melting point of about 15° C.

Preparation of the Tellurium Sulphoxide.—Sometimes we distilled the sulphur trioxide over into the tellurium, but we found it preferable to pour the oxide on to the metal, because in this way we could ensure contact of all the particles of the latter with the former. The two substances remain in contact for a short time without reaction, and for a longer time if the mixture is cold enough. The reaction takes place with distinct evolution of heat, and becomes visible by conversion of the loose grey tellurium into the more bulky, deep red, coherent sulphoxide. The supernatant trioxide in excess remains quite colourless, as observed by Weber. The reaction appears to be complete in a few moments after it has set in. The new solid having

been digested in the liquid oxide for some time at a temperature of 30—40°, the latter was drained off into the other receptacle and this was sealed off. The other sealed end was connected with a Sprengel pump, and its point broken off within the caoutchouc tube. The sulphur trioxide adhering to the tellurium compound was then removed, as completely as possible, by letting the mercury fall for an hour, while the tube holding the sulphoxide was immersed in water at about 35°. A long tube packed with borax and drawn out at each end, and interposed between the pump and the preparation-tube, served very effectively to arrest any sulphur trioxide. Potassium hydroxide, used at first instead of borax, was acted upon so violently as to melt and sometimes choke the tube. The preparation-tube was finally detached momentarily from the pump, so as to admit air, and its open end was then sealed.

Properties and Composition of Sulphoxide.—The sulphoxide, thus prepared, is an amorphous solid, which softens without melting at about 30°. It is of a beautiful red colour, and transparent in very thin layers. So far, it is just as Weber has described it. It is finely vesiculated, in consequence of the vaporisation within its substance of the excess of sulphur trioxide at first mixed with it. This vesicular state lightens the shade of the redness of the substance, and the walls of the vesicles are so thin as to make the surface of the mass iridescent.

Weber (*loc. cit.*) describes it as being very unstable, decomposing even in sealed tubes at ordinary temperatures, and yielding sulphur dioxide.* But, according to our experience, it appears to be quite stable at ordinary temperatures in the closed tube when pure, neither changing colour nor evolving sulphur dioxide.† During its preparation and purification, also, no sulphur dioxide was produced, when the sulphur trioxide was quite anhydrous. The sulphoxide does, indeed, sometimes slowly decompose when left in the crude state, its red colour assuming a brown shade, and then, too, sulphur dioxide is formed. We have not succeeded in determining the conditions of the occurrence of this change. Possibly it depends upon the sulphur trioxide used not being quite anhydrous. At one time we thought that it might be due to this action of light, but experiment has not confirmed our supposition.

* And tellurium also, according to the abstract in this Journal, but if so it must yield either tellurium dioxide or sulphur trioxide as well.

† A specimen of it, prepared on or about January 18th, will be laid before the meeting at which this paper is read, and it will be interesting to see whether it has remained unchanged during an interval of some months and a journey half round the world. [The specimens received from the authors, judging from their description, are unaltered.—Henry E. Armstrong.]

We have several times analysed the red sulphoxide, but only in one case have we found it to contain exactly the quantity of sulphur trioxide indicated by the formula SO_3Te, all the analyses giving an excess of SO_3. This one case, however, assuming the absence of error in our analysis, must be regarded as establishing its composition. The excess of sulphur trioxide in the other cases was most probably due to a retention of some of this substance within cavities in the viscid mass. Weber assigns to the sulphoxide the composition as we indicated by the above formula, having obtained in one case the calculated quantity of tellurium, in another a very little less than this. He purified his preparations from sulphur trioxide by pressing the warm viscid masses with a glass rod. This method of purification proved impracticable in our hands.

The details of our analyses are as follows:—The weight of tellurium used was taken before converting it into the sulphoxide; one point of the sealed tube containing the purified sulphoxide having been scratched with a file, the tube was weighed, its point cracked off, and the open end immersed in a dilute solution of bromine and hydrochloric acid. Very gradually this solution was allowed to act on the sulphoxide, so as to avoid loss by violent action. The tube, having been washed out and dried was weighed; the difference between the two weighings gave the weight of the sulphoxide, and the difference between this and the weight of the tellurium, gave the weight of the sulphur trioxide; but to make certain of the absence of water or any other foreign matter, the telluric acid in solution was reduced to tellurous acid by boiling with hydrochloric acid, and the sulphuric acid precipitated by barium chloride and weighed. These were the results:—

	I.	II.
Tellurium	0·6510	0·4862
Sulphur trioxide	0·4608	0·3020
Sum	1·1118	0·7882
Tellurium sulphoxide ..	1·1113	0·7885
Difference	−0·0005	+0·0003

The following are the percentage quantities calculated:—

	I.	II.	SO_3Te.
Tellurium.....	58·58	61·66	61·54
Sulphur trioxide	41·46	38·30	38·46
			100·00

β-Tellurium Sulphoxide.

When red tellurium sulphoxide is heated sufficiently, its colour changes to a bright fawn-brown. Prolonged heating in a vacuum even at 35° effects this change, but so very slowly that no change can be perceived, even after the lapse of an hour. At higher temperatures the transformation is more rapid, and at 90° almost instantaneous. No gas is evolved, and besides the striking change of colour, nothing else is observable. The vesicular condition remains just as it was, even to the iridescence of the superficial vesicles.* Heated to 130°, it softens and shrinks, its vesicular structure collapsing. Its brown colour is now of a deeper shade, owing to the absence of the vesicles. Heated to 180°, it again changes colour, and again becomes vesiculated, this time from evolution of sulphur dioxide. The mass becomes eventually black and solid on further heating, and now consists of the tellurium monoxide, described by us in another paper, the decomposition being almost complete at about 230°. The earlier effects of heating the red sulphoxide under atmospheric pressure do not appear to differ essentially from those of heating in a vacuum.

We have analysed this brown substance in the same way as the red, and find that it has the same composition. The results were:—

	I.	II.	III.
Tellurium.....	0·5829	0·1709	—
Sulphur trioxide.....	0·3715	0·1070	0·3178
Sum	0·9544	0·2779	
Tellurium sulphoxide..	0·9548	0·2780	
Difference ..	+0·0004	+0·0001	

In III we had not weighed the tellurium before making the sulphoxide. Calculating from the above numbers we get—

	I.	II.	III.	Mean.	SO_3Te.
Tellurium	61·04	61·47	—	61·26	61·54
Sulphur trioxide ..	38·91	38·53	37·90	38·45	38·46
					100·00

The brown sulphoxide now described remains unaffected when digested with liquid sulphur trioxide. But like the red sulphoxide, it dissolves readily in sulphuric acid, without evolution of sulphur dioxide, and yields the usual deep amethyst-red solution. In its behaviour with water, no difference from the red sulphoxide has been

* A specimen of the brown sulphoxide accompanies this paper.

observed, if we except a somewhat more violent action in the case of the red, perhaps due to the presence of a little sulphur trioxide in the preparation so tested.

As remarked in our paper on tellurium monoxide, the sulphoxide of tellurium yields with water free tellurium, the monoxide, tellurous acid, sulphurous acid, and sulphuric acid. A quantitative examination of this reaction has shown us that much more than half the tellurium is reduced to the elemental state.

The equations—

$$SO_3Te + H_2O = Te + SO_4H_2,$$
$$SO_3Te + H_2O = TeO + SO_3H_2,$$

and secondarily—

$$2TeO + H_2O = Te + TeO_3H_2,$$

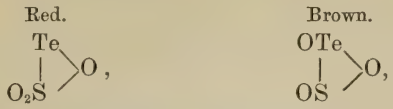
under the influence of the sulphuric acid formed, may serve to show how the products can be derived from the sulphoxide, and the elemental tellurium be in excess. But a satisfactory theory of the change has not presented itself to us. Even if the occurrence of the monoxide among the products be disregarded, and the equation

$$3H_2O + 2SO_3Te = Te + TeO_3H_2 + 2SO_3H_2$$

be adopted, the production of excess of tellurium, and of the sulphuric acid remains inexplicable, since sulphurous acid has no reducing action upon tellurous acid either alone or in presence of sulphuric acid, hydrochloric acid being required. We are strongly inclined to hold that the decomposition, $SO_3Te + H_2O = TeO + SO_3H_2$, is the primary one, although this assumption does not remove all the difficulties.

We do not think that the problem of the constitution of the sulphoxide receives any solution from the existence of its two modifications and their conversion into the monoxide. The monoxide does appear to be a base, and does not enter into chemical combination with other substances, while the modifications of the sulphoxide do not exhibit any differences in their few known reactions. If the sulphoxide is a sulphite, it is strange that it should dissolve in sulphuric acid without giving off sulphurous acid. Further, if it is a sulphite, it should be in the same series of tellurium compounds as tellurium monoxide, and there should be a corresponding hypotellurous sulphate, SO_4Te, formed from tellurium monoxide and sulphuric acid, which is not the case. As described elsewhere, the monoxide does dissolve in sulphuric acid, but it is at the same time converted into dioxide and—in solution in the acid—the red compound, which we must now regard with more certainty than before as the sulphoxide itself, and not a sulphuric compound corresponding with it.

We think that, for the present, the most probable formulæ of the sulphoxide in its two modifications, are—



which represent the red modification as a sulphonate of tellurium in the unstable condition of bivalency, and the brown modification as a better balanced combination of oxides of the two elements, in which both are quadrivalent, and the combination, therefore, more stable under rise of temperature than the red modification, and yet a combination out of which the tellurium cannot be expected to separate from the sulphur without reduction at the same time to a state of lower valency. If we had not Weber's evidence of the non-existence of two modifications of sulphur trioxide, we might connect these with the two modifications of tellurium sulphoxide.

Two quite distinct modifications of selenium sulphoxide appear to exist. We are at present examining them.

XLII.—*On a New Reaction of Tellurium Compounds.*

By Edward Divers and M. Shimosé.

Sulphuric acid can hold in solution only small quantities of tellurium dioxide, or its sulphate. But this solution can be made to furnish a reaction for tellurium of considerable delicacy. By pouring some of it into a hydrogen apparatus containing zinc and dilute sulphuric acid, and passing the escaping hydrogen, which will contain hydrogen telluride, through some more of the telluretted sulphuric acid, undiluted with water, the red colour of tellurium sulphoxide is rapidly developed in the previously colourless liquid—

$$2TeH_2 + TeO_2 + 3SO_4H_2 = 3SO_3Te + 5OH_2.$$

If the current of telluretted hydrogen be continued long enough, the red sulphoxide is destroyed, and a brown, insoluble substance produced in its place, which sometimes appears as scaly or crystalline black particles, with metallic lustre. This destruction of the sulphoxide can only be a result either of its deoxidation, or of its decomposition into sulphur trioxide and tellurium, the latter forming with the hydrogen telluride, a pertelluride. The much more probable change of deoxidation will be attended with the formation of sulphur dioxide,

while the other change will not. The quantities of tellurium compounds engaged being so very small in comparison with those of the sulphuric acid and the hydrogen, the sure detection by smell of any sulphur dioxide can hardly be expected. But by passing the gases through potassium permanganate solution, the sulphur dioxide which they contain can be very distinctly found as sulphate in the solution. In contrast with this, no sulphur dioxide can be detected in this way in the escaping gases during the production of the red sulphoxide, by the primary action of the hydrogen telluride. Telluretted hydrogen has no action upon pure sulphuric acid—at least, no immediate action; and pure hydrogen has no action upon telluretted sulphuric acid.

The brownish-black precipitate cannot well be elemental tellurium, for one reason, because of its brown colour, but mainly because tellurium is soluble in sulphuric acid in just that form from which it would in this case be produced. The precipitate does, indeed, redissolve in sulphuric acid, but only under certain conditions.

Thus it quickly redissolves with red colour in sulphuric acid containing tellurous sulphate. Less markedly, it also redissolves on adding fresh sulphuric acid to its mother-liquor. In this case, the sulphuric acid probably exercises an oxidising power by containing traces of dissolved oxygen, or oxidising agents. It redissolves in its own mother-liquor when the mixture is exposed to the air, the dissolution proceeding from the surface of the liquid downwards, evidently a case of atmospheric oxidation. But it also redissolves slowly when sealed up with its mother-liquor in glass tubes in an atmosphere of hydrogen, and this dissolution of it is accompanied by reduction of sulphuric acid; for on opening the tubes, the smell of sulphur dioxide is distinct. This reduction of sulphuric acid further shows that the precipitate is not tellurium, as this substance dissolves without forming sulphur dioxide.

We are led by the above properties of this brownish-black substance to regard it as a pertelluride of hydrogen, the hydrogen of which is readily oxidised by air, in presence of sulphuric acid, and more slowly, by sulphuric acid alone, with production of sulphur dioxide.

Not only is hydrogen pertelluride slowly oxidised by sulphuric acid, but the red sulphoxide is itself similarly affected. Sulphuric acid coloured deep red by tellurium sulphoxide dissolved in it, slowly bleaches, even in sealed tubes. That it does so when heated, is a fact quite familiar. On opening the sealed tubes when the bleaching has occurred, the odour of sulphur dioxide is quite apparent. The equation—

$$SO_3Te + SO_4H_2 = 2SO_2 + OH_2 + TeO_2,$$

expresses this change, the tellurium dioxide, no doubt, forming a sulphate with additional sulphuric acid.

When hydrogen containing hydrogen arsenide or phosphide, or selenide, is passed through sulphuric acid containing tellurous sulphate, the sulphuric acid also becomes coloured tellurium-red, and then bleaches, with the production of dark brown precipitates, or, in the case of the phosphide, a black precipitate.

Selenious oxide dissolved in sulphuric acid gives reactions corresponding with those of tellurium dioxide, but much less readily, and with much less striking colour-changes.

XLIII.—*Contributions to the Chemistry of Tartaric and Citric Acid.*

By the late Beaumont J. Grosjean, Chemist to Sir J. B. Lawes' Citric and Tartaric Acid Factory, Millwall: compiled from the Author's Manuscripts by R. Warington.

A word of preface is perhaps necessary. Mr. Grosjean was associated with myself for five years, 1870–75, in the Laboratory at Millwall, and he remained there as sole chemist from Midsummer, 1875, till his death on June 11th, 1882. During this time he conducted with great care many investigations, both on methods of analysis and on processes of manufacture. A paper "On the Determination of Tartaric Acid in Lees and Inferior Argol, with some Remarks on Filtration and Precipitation," was communicated by him to the Society in April, 1879. The greater portion of his results remained unpublished; they were, however, for the most part fairly written out in the form of Reports. From these Reports, from letters, and from the Laboratory Note-books, I have, with the consent of Sir J. B. Lawes, prepared the following abstract of a portion of his results:—

Different Rate of Loss of Different Specimens of Citric Acid in Dry Air.

In my own earlier experiments (*Chem. Soc. J.*, 1875, 928) the different behaviour of different samples of powdered citric acid had already been noticed. In some cases the crystallised citric acid lost the whole of its water when placed over oil of vitriol for 4—6 days; in other cases nothing was lost in five days. Mr. Grosjean afterwards met with similar results. In one instance he was fortunate in commencing on the same day determinations of water in three specimens of citric acid, which, as the experiment progressed, proved to be of

different characters. Specimen A was a fine crystal obtained from Mr. D. Howard. Specimen B was a part of fine crystals made at Millwall. Specimen C had been obtained by recrystallising B in the laboratory. All the crystals were freed from any adhering moisture with blotting-paper, and then powdered. Of A, 3 grams, and of B and C 1 gram were taken. Specimens B and C were placed in the same desiccator; A in another, standing by the side. Both desiccators contained fresh oil of vitriol, sp. gr. 1·845. In the following table will be found a selection from numerous successive weighings of the three specimens. The experiment commenced on April 21st, 1880 :—

TABLE I.—*Gradual Loss of Water by three Specimens of Citric Acid Crystals in Dry Air.*

Date of weighing.	Days since commencement.	Total loss per 100 of original weight.		
		A.	B.	C.
April 23	2	0·00	0·00	0·70
„ 27	6	0·10	0·35	5·55
„ 30	9	0·23	1·40	7·60
May 4	13	0·52	4·25	8·50
„ 6	15	0·68	6·25	8·55
„ 11	20	1·12	8·05	—
„ 15	24	1·75	8·55	—
„ 22	31	2·85	—	—
„ 28	37	4·38	—	—
June 4	44	5·35	—	—
„ 12	52	7·92	—	—
„ 21	61	8·47	—	—

The theoretical amount of water in citric acid crystals is 8·57 per cent.

The very different degree of tenacity with which water is held in different citric acid crystals is probably connected with some difference in the structure of the crystals, determined by the conditions prevailing during crystallisation. It is clear from the above results that when the molecular structure has been weakened by the loss of some water, the crystal parts with a considerable portion of the remainder with comparative ease; the last portions of water are, however, lost with great slowness.

Determinations of Citric Acid in Lemon and other Juices.

The value of lemon juice has usually been determined from its acidity. Besides the free acid a certain amount of combined organic acid is also present (*Chem. Soc. J.*, 1875, 931). The whole of the free and combined acid in lemon juice is not, however, citric acid. The

method employed in the Millwall Laboratory for determining the amount of citric acid present, or rather the amount of organic acid capable of yielding an insoluble calcium salt, has been already described (*ibid.*, 934). The juice is exactly neutralised with soda, an excess of calcium chloride added, and the calcium citrate precipitated by boiling in a salt or glycerin bath. The precipitate is collected and washed with hot water. The filtrate and washings are neutralised with dilute ammonia, and concentrated in the bath to a small bulk; the second precipitate thus obtained is also collected and washed. Mr. Grosjean was in the habit of concentrating yet a second time, and collecting a third precipitate, if any. The precipitates are finally ignited, and the citric acid originally present calculated from the neutralising power of the resulting carbonate of calcium. Working in this way, with 1 gram of citric acid, Mr. Grosjean obtained 99·6 per cent. of the acid taken.

In the following table will be found determinations of free acid, and of precipitable acid, made by Mr. Grosjean in commercial samples of concentrated lemon and other juices; the acid found is in all cases calculated as citric acid:—

TABLE II.—*Determinations of free and precipitable Acid in concentrated Lemon and other Juices.*

	Specific gravity of juice.	Acid, reckoned as citric (ozs. per gallon).		Precipitable for 100 of free acid.
		Free acid.	Precipitable acid.	
Lemon juice—				
Highest	1·235	61·2	63·4	103·6
Lowest	1·240	64·8	61·9	95·5
Mean of 895 pipes	1·241	62·1	61·6	99·2
Sample A	1·240	65·8	59·7	90·7
„ B	1·235	64·9	55·7	85·8
Bergamot juice—				
Highest	1·235	47·9	48·5	101·4
Lowest	1·235	52·3	49·9	95·4
Mean of 90 pipes	1·237	50·1	49·3	98·4
Lime juice—				
Sample A	1·326	108·3	99·8	92·2
„ B	1·205	59·2	53·9	91·1
Orange juice—				
Sample A	1·400	16·8	11·6	69·0
„ B	1·350	11·7	8·0	68·4

It appears from the above figures that the precipitable acid in commercial concentrated Lemon juice is, on an average, very nearly equal

in quantity to the free acid present; in 65 analyses, representing 895 pipes, the precipitable acid averages 99·2 per cent. of the free. There is, however, occasionally a somewhat considerable range of variation, as will be seen from the figures showing the highest and lowest proportion of precipitable acid found in the 65 samples. In two exceptional samples of juice, A and B, representing together 27 pipes, the proportion of precipitable acid is much lower; and in one sample, representing 25 pipes, not mentioned in the table as it seemed to lie intermediate between lemon juice and bergamot, the precipitable acid was only 81·1 per cent. of the free. There can be no doubt, therefore, that the method of precipitation ought to be adopted in all valuations of commercial lemon juice.

The analyses of concentrated Bergamot juice are much fewer; the proportion of precipitable to free acid appears very similar to that in lemon juice.

There are only two analyses of concentrated Lime juice; both show a distinctly low proportion of precipitable acid, a result confirmatory of the analyses already published (*Chem. Soc. J.*, 1875, 936).

The two specimens of concentrated Orange juice show, as we should expect, a very small amount of free acid. This acid is also to a considerable extent not citric, the acid precipitable as calcium salt bearing a smaller proportion to the free acid than in any of the other juices analysed.

The figures in the table clearly show that specific gravity is no guide to the value of juice. All lemon juice is brought as nearly as possible to the standard gravity of 1·24 for the purposes of sale.

Influence of Heat on Solutions of Tartaric Acid.

That crystallised tartaric acid when fused at 170° is converted into metatartaric, and at a higher temperature, or by longer heating, into ditartaric acid, is well known. According to Gmelin, the change into metatartaric acid may be effected in the presence of a small quantity of water; 2 or 3 parts to 60 of acid. Some of my own experiments with the tartaric liquors of the factory (*Chem. Soc. J.*, 1875, 988) had made it probable that the same change may to some extent occur when solutions of tartaric acid are concentrated in the ordinary way over steam, as it was found that two such liquors, when diluted and boiled for three hours, yielded 3·36 and 3·68 per cent. more of tartaric acid than before boiling. Mr. Grosjean has now amply proved that solutions of tartaric acid, concentrated on a water-bath, may undergo conversion into metatartaric acid to a very considerable extent. He has also shown that in a dilute solution, the reverse change, even in the cold, will slowly take place.

I. 40 grams of tartaric acid were dissolved in water, concentrated

in a beaker over a water-bath till a crust formed on the surface, and maintained four hours in this condition; the temperature of the tartaric solution was 93°. When cold, the whole was redissolved and brought to a litre. The acidity was now 97·9 per cent. of the original; while the tartaric acid, found by precipitation with citrate of potassium, was only 74·6 per cent. of the tartaric acid taken. On boiling a portion of the diluted solution for two hours, the acidity was raised to 99·9 per cent., and the tartaric acid also to 99·9 per cent. of the original acid, showing that a complete reversal of the reaction had been effected.

The remainder of the diluted solution which had not been boiled was mixed with a little phenol, and the amount of tartaric acid determined from time to time with the following results:—

Aug.	24, 1881,	tartaric acid	74·6	per cent.	of original acid.
„	25	„	77·2	„	„
„	31	„	81·7	„	„
Sept.	16	„	88·0	„	„
Oct.	18	„	90·0	„	„

The experiment now ceased for want of material.

II. 80 grams of tartaric acid were treated as before, the heating being continued $3\frac{1}{2}$ hours after a crust had formed; the temperature of the solution was 92°. When cold, the beaker was weighed. Assuming that it still contained 80 grams of tartaric acid, the water present was 24·75 grams. Redissolved and diluted to one litre, the acidity was found to be 97·7 per cent. of the original tartaric acid. Phenol was added, and the proportion of tartaric acid determined from time to time in the unboiled solution, with the following results:—

Sept.	23, 1881,	tartaric acid	84·3	per cent.	of original acid.
Oct.	18	„	88·0	„	„
Nov.	25	„	92·2	„	„
Jan.	6, 1882	„	96·2	„	„
Feb.	9	„	96·7	„	„

It will be noticed that the reconversion in the cold took place at first with some rapidity, but afterwards at a diminishing rate. In neither experiment is it absolutely completed, although in the last experiment the observations extended over 137 days.

With tartaric liquors containing a considerable amount of sulphuric acid, Mr. Grosjean found a smaller production of metatartaric acid on heating. The following experiment, save for the presence of sulphuric acid, is a duplicate of Experiment II.

III. 80 grams of tartaric acid were dissolved in water, with 16 grams of oil of vitriol; the solution was heated in a beaker on the water-

bath till a crust formed; heating was then maintained for $3\frac{1}{2}$ hours; temperature, 92—94°. When redissolved the acidity had diminished to 97·6 per cent., and the tartaric acid to 90·2 per cent. of the tartaric acid taken.

Mr. Grosjean has further confirmed my earlier results respecting the presence of metatartaric acid in factory liquors. In one liquor he obtained an increase of 6·4 per cent. of tartaric acid by dilution and boiling; while in another old liquor the increase following this treatment was 7·6 per cent. In a third instance the metatartaric acid did not amount to more than 1 per cent. of the total tartaric acid. Ditartaric acid was not found in any case.

Influence of Sulphuric Acid on the Crystallisation of Tartaric Acid.

The presence of much free sulphuric acid considerably diminishes the solubility of tartaric acid at ordinary temperatures. When to a saturated aqueous solution of tartaric acid half its volume of oil of vitriol is added, and the mixture cooled and stirred, an abundant separation of tartaric acid takes place. There is also apparently a greater difference between the solubility at high and low temperatures when sulphuric acid is present. A hot saturated solution of tartaric acid in water will deposit about 50 per cent. of its tartaric acid on standing in the cold a few days. A hot solution of tartaric acid in 1 volume of water, and $1\frac{1}{2}$ volume of brown oil of vitriol (sp. gr. 1·713), deposited 70 per cent. of its tartaric acid on standing. The mother-liquor, amounting to 260 c.c., contained only 30 grams of tartaric acid. The free sulphuric acid, always present in crude tartaric liquors, though in other ways injurious, thus allows a greater proportion of the acid to be obtained by a single crystallisation. The above observations were made in 1881.

XLIV.—*Note on a Basic Ammonio-copper Sulphate.*

By Spencer Umfreville Pickering, B.A. Oxon, Chemical Lecturer at Bedford College.

In a paper on the basic sulphates of copper (*Chem. News*, **47**, 182), the author stated that on dilution of a solution of ammonio-copper sulphate a basic precipitate is thrown down, containing only traces of ammonia. This holds good for solutions of the strength there named (0·02165 grams CuO per c.c.); with stronger solutions, however, the results are different.

To a nearly saturated solution of copper sulphate ammonia was added till the precipitate at first formed was almost entirely dissolved; the solution then contained 0·114 gram CuO per c.c., and corresponded in composition to $CuSO_4,3NH_3$.

This solution, on standing, continued for about a month to form a dark violet-blue deposit, and subsequently gave the following numbers on analysis :—

$$CuO = 32·544,\ SO_3 = 39·482,\ NH_3 = 27·974 \text{ per cent.},$$

corresponding to $4CuO,5SO_4,16NH_3$, which contains—

$$CuO = 31·984,\ SO_3 = 40·486,\ NH_3 = 27·530 \text{ per cent.},$$

but consisting probably of $CuSO_4,4NH_3$, contaminated with small quantities of neutral copper and ammonium sulphates.

On diluting this solution with comparatively small quantities of water, either before or after it had attained a constant composition, a more or less compact dark violet-blue precipitate gradually formed, which was found, like that deposited from the undiluted solution, to consist of $CuSO_4,3CuO,2NH_3,5H_2O$, while with larger quantities of water the precipitates were lighter in colour and more bulky, being similar to those described in the paper already alluded to. The precipitates containing ammonia when exposed to air soon attained a constant weight, but since they are slowly decomposed by water, small quantities only can be dried thus without decomposition. They varied considerably in colour and compactness. The accompanying table contains the results of various analyses, but, as some of the experiments were performed while the solution was altering in strength, the results, as far as column 1 is concerned, are not strictly comparable with each other. The ammonia was determined by distillation and Nesslerising.

The sulphate $CuSO_4,3CuO,2NH_3,5H_2O$ is but little affected by prolonged exposure to dry carbon dioxide, but in the moist state is soon converted by it into carbonate. On digestion with cold water for some days it is decomposed into copper oxide and ammonium sulphate.

A sample, on being heated in a current of dry air, began to be attacked at about 13° C., and after being heated at 100° C. for 20 hours, attained a constant weight, after which it gave the following numbers on analysis :—

$$CuO = 66·946,\ SO_3 = 16·987,\ NH_3 = 4·561,\ H_2O = 11·506 \text{ per cent.},$$

consisting probably of $CuSO_4,3CuO,3H_2O$, which contains—

$$CuO = 67·691,\ SO_3 = 17·116,\ NH_3 = 3·646,\ H_2O = 11·548 \text{ per cent.}$$

Molecules of water added to each mol. of CuO.	The anhydrous substance contained			The hydrated substance contained H_2O per cent.	Proportion of CuO to CuO + SO_3 per cent.	Remarks.
	CuO.	SO_3.	NH_3.			
1.	72·288	17·652	8·060	17·371	80·798	From the undiluted solution after 2 days } Dark part.
2.	73·818	18·128	8·054	17·285	79·845	From the undiluted solution after 2 days } Light part.
3.*	75·774	17·411	6·815	17·836	81·315	From the undiluted solution after 5 days.
4. 355	73·245	18·258	8·497	16·278	80·047	Dark part.
5.* „	74·500	18·000	7·500	18·141	80·541	Light part.
6. 520	73·133	18·316	8·551	16·687	79·971	Darkest part.
7. „	—	—	—	—	79·758	„
8. 1,350	86·129	12·164	1·715	18·237?	87·625	
9. 4,400	91·300	8·645	0·056	26·916	91·350	
10. 1,520	—	—	0·004	—	89·363	
11. 6,000	—	—	nil	—	91·180	
12. 35,000	—	—	nil	—	92·498	
13. Various	73·983	18·168	7·849	17·116	80·284	Mixed dark precipitates.
	73·293	18·104	8·202	16·957	80·189	Mean of 1, 2, 4, 6 and 13.
	73·449	18·548	7·917	17·285	79·818	Theory for $CuSO_4,3CuO,2NH_3,5H_2O$.

* Slightly decomposed in drying.

On being heated to a red heat it left a residue of cuprous oxide, a secondary product, no doubt, due to the reducing action of the ammonia evolved.

XLV.—*Note on the Action of Sulphuric Acid (sp. gr. 1·84) upon Potassium Iodide.*

By Herbert Jackson, Daniell Scholar, King's College, London.

Although it has been known for some time that when strong sulphuric acid acts upon potassium iodide, there are produced hydric sulphide, sulphur dioxide, iodine, hydriodic acid, hydropotassic sulphate, and water, in proportions varying according to the conditions of the experiment, still there have been no details published concerning the amounts produced in the different reactions.

It was therefore deemed interesting to obtain uantitative evidence as to whether definite reactions took place, and it was found that two occurred, one when the sulphuric acid was present in large excess, and the other when there was just sufficient sulphuric acid to satisfy the potassium iodide used in the experiment.

Under the conditions first mentioned it was found that all the iodine was liberated together with its equivalent of sulphur dioxide; hydropotassic sulphate and water being produced at the same time, according to the equation—

$$2KI + 3H_2SO_4 = 2I + SO_2 + 2KHSO_4 + 2H_2O.$$

Under the second conditions it was found that all the iodine was liberated, together with its equivalent of hydric sulphide; hydropotassic sulphate and water being at the same time produced, according to the equation—

$$8KI + 9H_2SO_4 = 8I + H_2S + 8KHSO_4 + 4H_2O.$$

In order to obtain both these reactions perfectly, it was found to be necessary to have the sulphuric acid boiling, so that the upper part of the vessel containing it should be filled with the vapour of sulphuric acid before bringing the two bodies into contact, so as to ensure the complete oxidation of the hydriodic acid which was first formed. The experiments were conducted in a glass tube fitted with a glass stopper, into which two small glass tubes were ground. The sulphuric acid was boiled in this tube, and the weighed potassium

iodide dropped into it during ebullition, the stopper being fitted in its place before any gas could escape.

The evolved gases were collected in a series of absorption-tubes, and any gas remaining in the first tube was swept out by a current of carbonic acid gas.

It was found that by judiciously arranging the length of the exit-tube, and keeping it cooled by water, none of the iodine passed into the absorption apparatus.

After the action was over, and the apparatus had cooled, the iodine was dissolved in carbon bisulphide, treated with calcium carbonate, to neutralise any free acid, and the iodine was determined by a standard solution of sodium thiosulphate. The following results were obtained:—

Iodine found.	Iodine required.
0·0701 gram	0·0708 gram
0·1816 „	0·1823 „
0·0643 „	0·0646 „

When the experiment was made with the sulphuric acid in large excess, the absorption-tubes were filled with water, and the dissolved sulphur dioxide determined by a standard solution of potassium permanganate. The following results were obtained:—

Sulphur dioxide found.	Required.
0·01516 gram	0·01525 gram
0·0077 „	0·0078 „

Under the second conditions named above, the water in the absorption-tubes was replaced by a standard solution of iodine and the hydric sulphide calculated by determining the amount of iodine converted into hydriodic acid. The following results were obtained:—

Hydric sulphide found.	Required.
0·007 gram	0·00662 gram
0·0061 „	0·00599 „

From these results it will be seen that the two equations given in the beginning of the paper represent the action taking place under the different circumstances; at the same time it is probable that the second reaction is the one which under any conditions occurs first, the sulphur dioxide being the result of the excess of the sulphuric acid upon the hydric sulphide. This is confirmed by the fact that however large the excess of sulphuric acid may be, hydric sulphide is always found in small quantities, unless the upper part of the tube containing it be filled with sulphuric acid vapour.

XLVI.—*Laboratory Notes.*

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.C.S., Lecturer on Chemistry in Dulwich College.

I. On the Action of Light and Heat on Cane and Invert Sugars.
II. On Hydroxylamine.
III. Recovery of Iodine from Organic Iodide Residues.
IV. A Residual Phenomenon of the Electrolysis of Oil of Vitriol.
V. On alleged Tests for Alcohol.
VI. Reaction of the Copper-zinc Couple on Nitric Oxide.
VII. On the Reducing Action of Spongy Lead.

I. On the Action of Light and Heat on Cane and Invert Sugars.

Nothing is more familiar to chemists than that living yeast-cells, and some other vegetable structures, are capable of resolving cane-sugar into alcohol and carbonic anhydride; and this decomposition is the more interesting as all attempts to bring it about by known chemical or physical processes have hitherto failed. We thought it worth while to try the effect of the copper-zinc couple at the ordinary temperature. The reaction did not take place in a 5 per cent. solution of cane-sugar: hydrogen was of course evolved (from the water), but no carbonic anhydride. At 100° C., however, carbonic anhydride was slowly evolved, and a small quantity of liquid distilled over, which gave iodoform on treatment with iodine and potassium hydrate, and acetic acid on treatment with potassium chromate and sulphuric acid. Our hopes appeared to be realised, but on examining the chemical change more fully, we found that the carbonic anhydride did not come from the sugar at all, and that the organic substance which distilled over was not alcohol, and was not dependent upon the couple for its formation. In fact, the carbonic anhydride arose from the splitting up of oxicarbonate of zinc, which is formed in the washing of the couple, and of which we had no previous knowledge; while the organic body is a product of the action of heat upon the sugar solution.

While investigating this subject, we made various observations regarding the influence of heat, light, germs, and air upon solutions of cane and altered sugar (glucose), and as they may help to clear up some of the contradictory statements that have been made upon this subject, we are induced to record the most important of them.

1. *The Action of Heat on an Aqueous Solution of Cane-Sugar.*

The usual mode of experimenting was to take a number of tubes with narrow tubules, of about 20 c.c. capacity, and nearly fill them with a solution of pure cane-sugar (5 grams to 100 c.c. of distilled water), which was then boiled for about five minutes in an oil-bath. To determine the effect of heat in absence of air, some of the tubes were sealed while the liquid was still boiling. About 15 c.c. of the solution in a sealed tube were exposed for 14 days to a temperature of 90° to 95° C.; it slowly became of a pale yellow colour, and was found to contain 3·6 per cent. of glucose, was acid to test-paper, and, on distillation, the iodoform-producing substance was detected. In another experiment the heating was prolonged to six weeks; the solution became much darker in colour, and contained some yellowish-brown matter, which readily dissolved in a solution of potassium hydrate, from which it was again precipitated on the addition of an acid. The solution was slightly acid, contained 2·8 per cent. of glucose, and yielded the iodoform-producing compound. It would appear, then, that nothing but an elevated temperature is necessary to convert an aqueous solution of cane-sugar into glucose and an acid body, with a minute quantity of an unknown volatile substance.

Experiments were made to ascertain whether the iodoform-yielding body is produced immediately from glucose, and whether carbonic anhydride accompanies its formation. 400 c.c. of a 5 per cent. solution, prepared carefully by ourselves, were boiled in a retort, and the distillate tested from time to time, and the substance we were in search of was detected in successive portions of the distillate; boiling water was added to the residue to make up the volume, and the air was driven out of the apparatus by a stream of pure hydrogen. The slow boiling was continued for 12½ hours, hydrogen passing through the apparatus, and subsequently through tubes containing baryta-water; the distillate contained, as before, a small quantity of the volatile compound, but no carbonic anhydride. It is evident, therefore, that the chemical reaction is essentially different from a vinous fermentation, and that the iodoform-yielding compound is not alcohol is also proved by its totally distinct odour, and the different volatility of its aqueous solution; it is not separated from water by potassium carbonate, and no other means have been found for its isolation.*

In our original experiments, in which the copper-zinc couple was heated to about 100° C. with cane-sugar solutions, only traces of

* Mr. Horace T. Brown has drawn our attention to a paper "On the Electrolysis of Sugar Solutions" in this Journal of July, 1872. He mentions an iodoform-producing body, which was probably the one here described, as he subjected his solution of glucose to distillation.

glucose were ever produced, even after the action had continued for weeks. This agent therefore prevents the conversion, probably by neutralising or destroying the acid compound as quickly as it is produced. It is remarkable also that a solution of cane-sugar remains colourless apparently any length of time, when heated with the copper-zinc couple.

2. *Influence of Light, Atmospheric Germs, and Air.*

It seemed of interest to examine some of the conflicting statements in regard to the conversion of cane-sugar into glucose. A number of the tubes previously described were very nearly filled with a 5 per cent. solution. Twelve were sealed, while the solution was boiling, and six of them were exposed to full daylight at ordinary temperatures, the other six being kept in the dark. Six more were opened to the air, the tubules being plugged with cotton-wool, and three of them were exposed to daylight, and sometimes to the direct rays of the sun, the other three being kept in complete darkness. Six others were prepared with the tubules open, three being exposed to the light, and three kept in the dark. After allowing the whole of these tubes to remain from December, 1877, to May, 1879, the solutions were examined for glucose and fungoid growths. The amounts of glucose found in the several experiments, are shown in the subjoined table:—

Nature of Experiment.	Grams of Glucose in 100 c.c.						
	I.	II.	III.	IV.	V.	VI.	Mean.
Solution boiled in tubes, but not exposed to light, &c.	0·0162	0·0185	0·0162	0·0168	0·0209	—	0·0177
In sealed tubes.							
(i). Exposed to light	0·0187	0·0116	0·0193	0·0160	0·0145	—	0·0160
(ii). In darkness	0·0145	0·0250	0·0152	0·0232	0 0203	0·026	0 0207
In tubes plugged with cotton-wool.							
(i). Exposed to light	0·0203	0·0193	0·0261	—	—	—	0·0219
(ii). In darkness	0·0246	0·0272	0 0262	—	—	—	0·0260
In open tubes.							
(i). Exposed to light	0·0366	0·0225	0·0490	—	—	—	0·0360
(ii). In darkness	0·0214	0·0325	0·0354	—	—	—	0·0297

As the very method of preparing these solutions produces about as

much glucose as was found in the tubes 17 months afterwards, the above results show that neither light nor air, singly or jointly, changes cane-sugar in aqueous solution at the ordinary temperature.

As Rouet (*Compt. rend.* for 1871, p. 1049) states that a solution of 10 grams of white cane-sugar in 50 grams of water, enclosed in sealed tubes from which the air had been expelled by boiling the liquid, and exposed for five months to light, was found to be half-converted into glucose, we made four experiments with solutions of this strength; and obtained substantially the same results as before.

All the solutions in the sealed tubes were found to be perfectly bright, and free from fungoid growths, as were those in the tubes plugged with cotton-wool and exposed to daylight. On the other hand, all the solutions open to the air contained white matter at the bottom of the tube and fungoid filaments in the liquid. In the tubes that were plugged with cotton-wool, but kept in the dark, a smaller quantity of white matter—about a millimetre in diameter—was found at the bottom of the liquid in each case. A microscopical examination of the white matter was kindly made by Dr. Lionel Beale, who reported that "the fluid contained abundant evidence of living organisms—micrococci, bacteroid bodies, and mycelial filaments."

It would appear then that light is detrimental to development of fungoid growths in a solution of cane-sugar exposed to atmospheric air.

II. On Hydroxylamine.

In our experiments on the reduction of nitrates we thought it not improbable that hydroxylamine might be found, and were led to make an observation or two upon that substance.

The Nessler reagent behaves with an aqueous solution of it in apparently the same manner as with an aqueous solution of ammonia, provided there be not more than 0·0002 gram in 100 c.c. of water; but if the solution is stronger, the visible effect is very different. The results are shown in the following table:—

Hydroxylamine in 100 c.c.	Appearance.
0·0004 gram	Blackish-brown opacity.
0·002 „	Reddish precipitate, slowly becoming black.
0·01 „	Reddish precipitate, becoming black at once.
0·02 „	Black opacity and precipitate immediately.

It was found that the copper-zinc couple was capable of reducing the hydrochloride of this base. In an experiment 14 c.c. of an aqueous

solution, containing 0·006 gram of the hydrochloride, were poured on to a small quantity of the couple (made from 125 square centimetres of foil, wet with water). In 30 minutes hydroxylamine disappeared, and ammonia was found in its place.

III. Recovery of Iodine from Organic Iodide Residues.

In the course of our work on the preparation of zinc ethers, &c., quantities of various organic iodides have been obtained, too impure for use, and therefore only of value for their iodine. The process we have employed now for some time for the recovery of this element from such residues is as follows:—

In the first place we transfer the iodine of the organic iodide to zinc by pouring the residues on an excess of copper-zinc couple wet with water or alcohol, and allowing sufficient time for the transference to be completed. It is well to attach an inverted condenser to the vessel, for some iodides undergo decomposition very rapidly with evolution of much heat. The residue is then digested with hot water to dissolve the zinc iodide, and the iodine may be separated by any one of the well-known reactions. We adopt that of bleaching powder, which, when performed on a pretty large scale, yields about 95 per cent. of the iodine actually present.

IV. A Residual Phenomenon of the Electrolysis of Oil of Vitriol.

In our study of the electrolysis of oil of vitriol (*Chem. Soc. Trans.*, 1879), we noticed that gas continued to be evolved from both electrodes for days after connection with the battery had been broken. In one case, where the acid had been subjected to the current for 48 hours, the following amounts of gas were collected in the limbs of the Hoffmann apparatus at the undermentioned times:—

Time.	Limb where H had been evolved.	Limb where O had been evolved.
1 day.	0·5 c.c.	2·8 c.c.
2 days.	1·8 „	7·8 „
3 „	5·1 „	12·2 „
5 „	9·1 „	16·8 „
7 „	12·4 „	19·8 „
9 „	14·4 „	21·5 „
13 „	16·6 „	22·2 „

In the first experiment, where the taps of the apparatus were open, the evolution of gas took place only at the electrodes, but in the one just detailed, where the taps were closed, gas was also noticed rising

in the reserve tube and occasionally from the liquid beneath the electrode in the hydrogen limb. This generation of gas was thought at first to arise from some electrochemical action; but on examination the gas in both limbs was proved to be nothing but oxygen, which at once negatived this supposition. On experimenting further it was found that the addition of a very small quantity of water to the acid which had surrounded the anode produced an evolution of gas, also that gas was slowly liberated from a plate of platinum immersed in the acid, and much more copiously by the metal in a fine state of division. These properties will be recognised as belonging to Berthelot's persulphuric acid, the presence of which fully accounts for not only the gas evolution at the platinum electrodes, but also that from the liquid in the reserve tube.

V. On Alleged Tests for Alcohol.

In the first of these notes we have shown that the formation of iodoform is not a certain test for alcohol. About the time of our experiments Mr. Davy communicated a note entitled "A New Test for Alcohol," which depends upon the fact discovered by him that alcohol strikes a beautiful blue colour with a warm solution of molybdic anhydride in oil of vitriol. On trial we found that the so-called test for alcohol was merely a test for a reducing agent. The following substances, among others, were found to give the blue coloration to the molybdic solution: Ammonium sulphide, ferrous sulphate, sodium sulphite, and formic acid. But, as we were more particularly concerned in the detection of alcohol in the presence of possible small quantities of sugar, the action of this latter substance was tried upon the test, when it was found that one drop of a 2 per cent. solution produced the blue coloration most distinctly. In 1805 Grotthus studied the electrolysis of this very molybdic solution, and noticed a blue coloration at the kathode, where it is known that reduction takes place.

VI. Reaction of the Copper-zinc Couple on Nitric Oxide.

It has been pointed out by Graham and others that hydrogen in the occluded condition is much more chemically active than when in its ordinary gaseous state.

We have already suggested that hydrogen, immediately after its liberation from water by the action of the copper-zinc couple, becomes more or less completely occluded by the spongy copper which constitutes the negative element, and that the reducing property of the couple arises from the presence of hydrogen in the occluded state. In continuation of our work on this subject we made the following

experiments on the action of the couple in the presence of water on nitric oxide :—

(i.) 30 litres of the gas were passed in 7 hours over 2000 square centimetres of zinc foil coated with 18 grams of black spongy copper, the couple being wet with water. 0·037 gram of ammonia was produced.

(ii.) In another experiment 26 litres of nitric oxide were passed in about 5 hours over 2500 square centimetres of zinc foil, coated with 20 grams of copper; 0·05 gram of ammonia was produced.

The question was now suggested, does free nitrogen also hydrogenise to ammonia under similar circumstances ? Several prolonged experiments were made, but no evidence was obtained of the formation of ammonia.

VII. On the Reducing Action of Spongy Lead.

In our recent experiments upon lead and lead peroxide batteries we were desirous of ascertaining whether spongy lead perfectly free from hydrogen was capable of reducing such salts as nitrate and chlorate of potassium. For this purpose spongy lead was prepared by precipitating the metal from the acetate by means of zinc, taking care that the salt was always in excess. It is difficult to imagine that lead prepared in this way should contain any occluded hydrogen. Nevertheless, it somewhat quickly reduced nitrate to nitrite of potassium. This action was found to be accelerated by heat, and to be retarded by the presence of sulphuric acid. A minute quantity of ammonia was also produced, especially when sulphuric acid was present or a high temperature employed.

In each of the experiments, the results of which are set out in the following table, 50 grams of spongy lead were employed, and 200 c c. of a 5 per cent. solution of nitre. In experiments III and IV the nitre solution contained 1 per cent. of H_2SO_4.

Experiment.	Temperature.	Time.	Percentages (grams).	
			KNO_3.	NH_3.
I.	13°	1 hour.	0·38	0·00005
„	„	24 hours.	2·06	0·00015
„	„	48 „	2·43	0·00024
II.	50	1 „	0·74	0·002
III.	13	1 „	0 05	0·006
IV.	50	1 „	0·13	0·003

Spongy lead has no action on an aqueous solution of potassium

chlorate, but in presence of 1 per cent. of H_2SO_4 its reduction to chloride takes place slowly at ordinary temperatures.

The increased chemical activity of substances, when in a finely divided condition, is to be generally accounted for by the greater surface exposed, and as a rule the actions brought about are similar in kind, but differ in degree. Spongy lead appears to form no exception. Ordinary lead filings were found to reduce nitre, &c., but very much more slowly.

XLVII.—*The Action of Nitrous Anhydride on Glycerol.*

By Orme Masson, M.A., B.Sc., Edinburgh University.

Some time ago Professor Crum-Brown observed that, when nitrous anhydride is passed into glycerol, the liquid gradually separates into two layers, and that one of these consists of a substance readily decomposed by water. Lately, his attention being again called to the subject, he very kindly asked me to investigate it.

I have employed the pure glycerol of commerce and nitrous anhydride generated from "porcelain arsenic" and nitric acid of sp. gr. 1·35. If the gas be passed direct into glycerol at the ordinary temperature, it is quickly absorbed, the liquid becoming yellow and losing its viscosity; and the temperature rises till decomposition sets in, causing a violent evolution of nitric oxide gas, which appears to continue so long as there remains any glycerol to oxidise. But if the gas be dried by passing it over fused calcium chloride, and the tube containing the glycerin be kept cool by surrounding it with cold water, the absorption goes on quite quietly and unattended by any evolution of nitric oxide.

The liquid increases greatly in bulk (from one volume to about two and a half) and in mobility; and its colour changes through various shades of yellow and brown, becoming dark green towards the end of the reaction. This point is easily ascertained: for the contents of the tube are seen to consist of two liquids of different refractive power, which are kept partially mixed only by the agitation caused by the bubbles of gas. The passage of nitrous anhydride should be continued for some little time after this, and may then be stopped, when the liquid at once divides into two layers. Of these, the smaller is an aqueous solution of nitrous acid and of oxidation products of glycerol which have, as yet, been only partly examined. The liquid which forms the larger layer consists of a *nitrous ether of glyceryl*, also containing nitrous anhydride and oxidation-products in solution.

It occupies about four times the volume of the aqueous layer, which is found sometimes above and sometimes below it, the relative densities being affected by the duration of the passage of the gas. The two layers should be separated as soon as the action is finished, as, when left in contact, they react on one another with evolution of nitric oxide.

Purification of the Nitrous Ether.—The following has been found the best means of freeing the liquid from the excess of nitrous anhydride and the oxidised substances which it contains in solution. It is placed in a distilling flask connected with a long condenser and a receiver, and having a tube fitted through its cork, and reaching to the bottom, which serves for the passage of a rapid current of gas. The whole apparatus, as well as the gas, must be perfectly dry. I have commonly employed hydrogen; but air would probably act as well. Large quantities of red fumes are at first carried away, through the condenser, by the gas current; and the liquid gradually becomes amber-yellow, but the colour does not diminish beyond a certain point. The flask is then gradually heated by means of a water-bath previously placed under it, the hydrogen current still continuing; and, at a temperature which varies with the rapidity of the current, the liquid begins to be carried over into the receiver. At the beginning of the distillation, a certain amount of red fumes is always formed; but their quantity is comparatively small, and they are quickly swept away by the hydrogen. The liquid is thus made to distil over, with but small decomposition, below 100°, or some 50° below its own boiling point. At the end a colourless viscous residue of oxidised matter is left in the flask. A second similar distillation yields a much smaller residue, and after two or three distillations it becomes practically *nil*, while the initial evolution of red fumes is also greatly reduced, if not entirely got rid of.

Analysis.—In comparing the figures obtained with each other, and with those calculated for the trinitrite, it must be borne in mind that the substance is one both difficult to obtain pure and extremely liable to decomposition afterwards. They agree, however, closely enough to show that it consists essentially of glyceryl trinitrite, and that it contains neither of the lower nitrous ethers. The nitrogen was estimated by Schlösing's method, the liquid being dissolved for this purpose in a measured quantity of glacial acetic acid.

Calculated for Glyceryl dinitrite.		Calculated for Glyceryl trinitrite.		Found.				
				I.	II.	III.	IV.	V.
C_3	24·00	C_3	20·11	19·99	19·59	19·39	—	—
H_6	4·00	H_5	2·79	4·00	4·10	3·96	—	—
N_2	18·66	N_3	23·46	—	—	—	22·31	22·53
O_5	53·33	O_6	53·63	—	—	—	—	—

Properties of Glyceryl Trinitrite.

The freshly distilled liquid is mobile and volatile, and of an amber-yellow colour. Very possibly it is colourless when quite pure; but I have not been able to obtain it so. It boils, with partial decomposition, at about 150° C., the distillate coming over green with nitrous anhydride; but if the red fumes which form at first be at once swept out with a current of dry gas, and this be then turned off, the greater part of the liquid will distil unchanged (150—154°), and the distillate will be of the usual colour. Experiment has shown that the previous distillations on the water-bath are absolutely necessary, as any attempt to distil the impure liquid at its own boiling point results in its total decomposition. These facts point to the conclusion that the liquid if quite pure would be capable of boiling without any decomposition. Its specific gravity, determined at 10°, is 1·291 (water at 15·5° = 1). It burns with a whitish flame, but does not explode under the hammer. It has a strong nitrous smell, due to the decomposition of its vapour, and exerts a bleaching action on the skin. It is soluble in ether, chloroform, and benzene, but insoluble in carbon disulphide. Cold glacial acetic acid dissolves it with a green coloration, and the solution evolves nitrous fumes when heated. The cold solution also slowly loses nitrogen when kept some time. Strong sulphuric acid attacks the trinitrite violently, with evolution of red fumes and of a colourless gas, and eventual charring. Dry hydric sulphide reduces it rapidly, with precipitation of sulphur and great evolution of heat. Potash-solution decomposes it to form potassium nitrite; but, at the same time, part of the nitrogen seems always to go off as nitric oxide. Crystallised urea acts on it violently: gas is evolved, and a colourless viscous liquid remains, which is presumably glycerol. Absolute alcohol decomposes it at once, with formation of ethyl nitrite.

The most marked property of the substance is its decomposition with water. The two liquids do not mix, but react on one another at their surface of contact, from which there rises a constant flow of bubbles of nitric oxide. The action is greatly accelerated by shaking or by the application of heat. If some of the liquid be heated with a large excess of water, nitric oxide is evolved in quantity, and the solution contains free nitric acid. If this be neutralised with potash, and the solution concentrated, a viscous liquid is obtained which is apparently glycerol; but if only a small quantity of water be employed, or if the liquid be evaporated without neutralising it, oxidation takes place, with formation of an acid which gives a lime salt insoluble in alcohol, presumably glyceric acid. The primary action of water, then, seems to be that it decomposes the glyceryl trinitrite into

glycerol and nitrous acid, which is again broken up by the excess of water into nitric acid and nitric oxide.

When exposed to the air, glyceryl trinitrite decomposes slowly, becomes green, and evolves nitric oxide, and after several days crystals of oxalic acid appear on the surface of the liquid and on the upper parts of the tube containing it. Probably the reason of this is that the atmospheric moisture liberates nitric oxide, which immediately takes up oxygen, parts with it, and takes up more, so that the surface of the liquid is constantly exposed to the attack of a strong oxidising agent.

It is impossible to preserve the liquid in the pure state, or, indeed, to keep it at all for any length of time, even though it be protected from the action of moisture by being sealed up in tubes immediately after distillation, for it rapidly decomposes, acquiring a dark green colour from liberated nitrous anhydride, and sufficient pressure is gradually accumulated to burst and shatter the glass tube. In this property it resembles ethyl nitrite. The spontaneous decomposition seems to take place more slowly in the dark than in daylight, but the relative rates have not been observed.

I am at present engaged in further investigation of this substance.

XLVIII.—*On the Preparation of the Pentathionates.*

By S. Shaw, Student in the Laboratories of the Owens College.

In a paper published in *Liebig's Annalen*, Bd. **213** [3], 329—363, Professor Spring denies that any results so far obtained possess sufficient authority to be accepted as proof of the existence of pentathionic acid, either in the free state or combined to form pentathionates. He combats the statement of V. Lewes, detailed in this Journal (**39**, 68), that he had prepared and analysed the potassium and barium salts of the acid in question, by relating his own lack of success in the attempted repetition of Lewes's preparations and analyses. Spring states that in attempting to prepare the potassium and barium pentathionates, in one case he obtained an impure salt containing more sulphur than a tetrathionate but less than a pentathionate, and in the other, crystals containing free sulphur, and dissolving in water to a turbid and acid liquid. He finally states it as his opinion that the so-called pentathionic acid consists of a solution of sulphur in tetrathionic acid, and that salts obtained from this acid are simply tetrathionates containing admixed sulphur.

The following experiments were undertaken, in accordance with Professor Roscoe's wish, for the purpose of testing the accuracy of Lewes' results. The first step taken was that of writing to Mr. Lewes, to invite him to send the exact description of the way in which he had operated in obtaining his preparations, and to this he cordially responded.

Sulphuretted hydrogen and sulphur dioxide gases were simultaneously passed into 3 litres of distilled water contained in a Winchester quart bottle, for about 32 hours, the sulphur dioxide being kept slightly in excess.

A normal caustic potash solution was prepared, and the Wackenroder solution obtained as above, without separating its suspended sulphur, was titrated with it. 10 c.c. of Wackenroder solution required 5 c.c. of normal potash solution for complete neutralisation, or 2·5 c.c. for half neutralisation. To 3000 c.c. of Wackenroder solution, 750 c.c. normal potash solution were added, slowly, and with continual stirring. After standing some time, the solution was filtered, the filtrate passing through perfectly clear. This clear filtrate smelt strongly of sulphur dioxide, and a portion treated with excess of potash failed to give any precipitate of sulphur, possibly because the sulphur at once passes into combination with the sulphurous acid existing in the liquid, and in presence of the alkali forms thiosulphate. The filtered solution was now evaporated on the water-bath, when sulphur was deposited and sulphur dioxide evolved, and on treating a portion with potash, an abundant precipitate of sulphur was obtained.

After concentrating on the water-bath, the liquid was placed in a partial vacuum over sulphuric acid, when in about eight days a crop of perfectly clear and transparent crystals was obtained, which on analysis proved to be anhydrous potassium tetrathionate.

	Salt taken. Gram.		K_2SO_4. Gram.	Percentage of potassium.		Calculated for $K_2S_4O_6$.
I.	0·768	gave	0·438	= 25·60	Mean = 25·76	25·87
II.	0·526	„	0·303	= 25·93		

		$BaSO_4$.	Percentage of sulphur.	
0·584	„	1·7857	= 42·0	42·35

On further standing, more tetrathionate crystals were deposited from the mother-liquor, and after some time a third crop was obtained. On examining this crop under the microscope, part of the crystals clearly resembled the previous crops, but amongst them were seen some crystals of quite different form. It was further found that if from this mixed crop a crystal, now recognised by the above analysis to be the tetrathionate, was carefully picked out, dried in a small piece of

filter-paper, placed in a watch-glass, dissolved in a little water, and then treated with a drop of caustic soda solution, not the slightest change appeared. The same process repeated in another watch-glass with a crystal of the different form, resulted in the immediate appearance of a white precipitate of sulphur.

Since all the crystals in this crop were perfectly transparent, and yielded perfectly clear and neutral solutions, there can be no question, simple though the method may be, that the former, being crystals of potassium tetrathionate, the latter must be those of a totally different and less stable substance, decomposed by alkali.

This mixed crop of crystals was analysed, and gave the following numbers:—

	Salt taken.		K_2SO_4.	Per cent. of K.	
I.	0·455	gave	0·2315	= 22·96	Mean = 22·91
II.	0·3375	„	0·172	= 22·87	

			$BaSO_4$.	Per cent. of sulphur.
I.	0·287	„	0·9082	= 43·45

or K : S : : 2 : 4·6

After some time, two other crops of mixed crystals were obtained, and these still showed on analysis the relation K : S :: 2 : 4·6.

Fourth Crop.

	Salt taken.		K_2SO_4.	Per cent. of K.	
I.	0·283	gave	0·153	= 24·2	Mean = 24·07 per cent. of potassium.
II.	0·268	„	0·143	= 23·95	

			BaS_4.	Per cent. of sulphur.
I.	0·245	„	0·802	= 44·93

or K : S : : 2 : 4·6.

Fifth Crop.

	Salt taken.		K_2SO_4.	Per cent. of K.	
I.	0·1515	gave	0·0785	= 23·25	Mean = 23·24 per cent. K.
II.	0·1830	„	0·0970	= 23·23	

			$BaSO_4$.	Per cent. of S.
I.	0·152	„	0·4815	= 43·50

or K : S : : 2 : 4·6

The next crop was composed of larger crystals, and the strange crystals were so abundant in quantity as to be easily discernible, and indeed a quantity was carefully selected and analysed, with the following result:—

	Salt taken. Gram.		K_2SO_4.	Percentage of potassium found.		Calculated for $K_2S_5O_6 + H_2O$.
I.	0·1595	gave	0·0785	= 22·08	Mean = 22·068	22·13
II.	0·052	,,	0·0255	= 22·057		

		$BaSO_4$.	Per cent. of sulphur.	
Gram.				
0·218	,,	0·7217	= 45·45	45·42

		H_2O.	Per cent. H_2O.	
Gram.				
0·2745	,,	0·0205	= 7·4	5·11
		or K : S : : 2 : 5·0		

The water of crystallisation was determined by combustion with lead monoxide, and the difficulty of excluding traces of moisture probably accounts for the difference between the found and calculated percentages of water.

These crystals thus analysed were *colourless* and *transparent*, and also dissolved in water to a perfectly *clear neutral solution*.

The following are the results of the analyses of all the crops obtained, ending with the analysis of the selected crystals of pentathionate:—

1st crop.....	K : S : : 2 : 4·0	
2nd ,, ...	K : S : : 2 : 4·0	
3rd ,, ...	K : S : : 2 : 4·6	mixed.
4th ,, ...	K : S : : 2 : 4·6	
5th ,, ...	K : S : : 2 : 4·6	
6th ,, ...	K : S : : 2 : 5·0	selected.

Mr. H. Baker kindly determined the crystalline form of both the tetra- and penta-thionate.

Examined microscopically the crystals of potassium tetrathionate and pentathionate are both seen to belong to the rhombic system, but differ entirely from each other, since the tetrathionate is most markedly hemimorphous, whilst the pentathionate is holohedral.

The general form of the tetrathionate is that of a thick but flat crystal, terminated at one end by a pair of slant faces meeting sharply in a point, at the other by a slant face at right angles to the length of the crystal. The depolarising directions are parallel and at right angles to the length, and in the polariscope one of the two optical axes is just visible.

The principal forms are $P\breve{\infty}$, P, and $P\bar{\infty}$ (no measurements having been made, the signs $\breve{}$ and $\bar{}$ are only used for distinction). Two faces of $P\breve{\infty}$ give the crystals their tabular appearance, and $P\bar{\infty}$ is the hemimorphous form. The plane of the optical axes is $\infty P\bar{\infty}$.

The pentathionate forms short thick prisms, four or six-sided, with

flat terminal faces and small subsidiary pyramidal or domal faces. Forms $\infty P . 0P . \infty P\breve{\infty} . P\breve{\infty}$. The depolarising directions are parallel and at right angles to the prism-edges. Other crystals showed more numerous faces, but could not be made out under the microscope.

It was observed, in the course of several attempted preparations of potassium pentathionate from half-neutralised Wackenroder solutions, that on evaporation even in a vacuum over sulphuric acid, sometimes the liquid persistently remained turbid, even after many filtrations, and the crystals obtained in such cases were contaminated with sulphur and quite unfit for analysis, exactly according with Spring's experience in his attempt to repeat Lewes' method of preparation. It is not easy to say in what respect the mode of conducting the preparation when pure specimens were obtained differed from that in which an impure and less stable product was the result.

XLIX.—*Note on Pentathionic Acid in connection with the foregoing Paper.*

By Watson Smith.

In the preparation of the Wackenroder solution by Mr. Shaw, to serve as material for the experiments he has detailed in the foregoing paper, it seemed of interest once more to determine whether this solution, as stated by Spring (*Annalen*, **213** [3], 352), when prepared so that sulphurous acid shall throughout the course of saturation be maintained in slight excess, really does or does not possess bleaching power for indigo solutions, and so set at rest an already sufficiently vexed question. Mr. Shaw, after scrupulously adhering to the condition specified above, viz., a maintained excess of sulphurous acid during saturation, obtained a Wackenroder liquid not bleaching even very dilute indigo solutions. He thus confirms the results of Smith and Takamatsu on this head.

Now the importance of a confirmation or otherwise of this reaction will be manifest when it is remembered that Spring (*loc. cit.*) bases upon it a theory for the formation of tetrathionic acid in the Wackenroder solution, according to which theory thiosulphuric acid ought simultaneously to be formed, and it is to the presence of this thiosulphuric that Spring ascribes the bleaching power referred to, which he states he has observed in the Wackenroder liquid. The equation Spring gives to illustrate the theory thus set up, and which must stand or fall by the success or failure of the reaction in question, is:—

$$(1)\ SO_2 + H_2O + S = HS.SO_3H.$$

$$(2)\ SO_2 + \left\{\begin{matrix}HS.SO_3H\\HS.SO_3H\end{matrix}\right. = H_2SO_2 + \left\{\begin{matrix}S.SO_3H.\\S.SO_3H\end{matrix}\right.$$

A circumstance well worthy of record was observed further, viz., that the Wackenroder solution as freshly prepared is not only precipitated by alkalis, but also by acids, sulphur in both cases being separated, whilst on the other hand, the half-neutralised solution is not precipitated by alkalis in excess, although a precipitation is formed by acids, sulphur and sulphur dioxide being set free. Moreover the liquid obtained after concentration and filtration of the half-neutralised solution, yields, on treatment with acid, no precipitate of sulphur whatever; but on treating with alkalis, yields a considerable precipitate. The following is the explanation of these apparently paradoxical results.

As is well known, a freshly prepared Wackenroder solution continues for a long time to deposit sulphur if left to itself, and if the mixed gases in the preparation have been passed into a saline solution (containing, *e.g.*, sodium, magnesium, or calcium chloride) far more sulphur is precipitated than would be the case if pure water had been used. Stingl and Morawski (*J. pr. Chem.* [2], **20**, 76), who demonstrated this fact, state that the cause of this action is a physical one, and the hastened precipitation on addition of hydrochloric or sulphuric acids is doubtless due to a similar cause. It is clear indeed from Stingl and Morawski's experiments that pure water should be used in the preparation of the Wackenroder solution, if an acid of maximum stability is to be obtained.

In explanation of the non-precipitation of the half-neutralised Wackenroder liquid by alkalis, and its precipitation by acids, it may be mentioned at the outset that this liquid smelt strongly of sulphurous acid, and that sulphur had abundantly separated out on half-neutralising. The Wackenroder liquid, consisting of a solution of pentathionic acid, on half-neutralising with the dilute alkali, yields—

1st. Alkaline pentathionates.

2nd. Alkaline tetrathionates, formed by subsequent decomposition of the pentathionate.

3rd. Alkaline thiosulphates and sulphites, formed by subsequent decomposition of the pentathionate.

4th. Free sulphurous acid and sulphur, the latter arising primarily from the disintegration of the pentathionic acid in forming tetrathionates, and both former and latter secondarily, from that of the thiosulphates in the slightly acid solution.

Now in presence of *excess of sulphurous acid*, no precipitate of sulphur appears in a solution of a pentathionate on adding an alkali

in excess, because the conditions are thus present for an immediate formation of thiosulphate, which accordingly takes place:—

$$2NaOH + S + SO_2 = SO_2.SNa.ONa + H_2O.$$

This fact is easily proved by experiment. Thus the apparently paradoxical result, by which the half-neutralised Wackenroder liquid is not precipitated by alkalis, is accounted for. The other part of the apparent difficulty remains to be explained, viz., why the solution, on evaporation and concentration, assumes a normal condition, that is, it is precipitated by alkalis, and afterwards yields crops of tetra- and penta-thionates. The explanation given is the following:—On evaporating the half-neutralised liquid, free sulphur dioxide is expelled, and sulphites and thiosulphates are rapidly and completely decomposed by the hot, though but slightly acid liquid, with separation of sulphur and evolution of sulphur dioxide. That such decomposition of sulphites and thiosulphates does take place on warming with excess of pentathionic acid, has been proved by experiment. Finally, a liquid is obtained free from sulphites and thiosulphates, and containing the tetra- and penta-thionates.

It thus appears that pentathionic acid in the free state is not only stable, but that when used in excess, and warm, it is capable of decomposing solutions of sulphites and thiosulphates, causing liberation of sulphur and sulphur dioxide; the pentathionates, which are thus formed being, however, more readily decomposed than the acid itself, will undergo partial decomposition into tetrathionates and sulphur.

L.—*Note on the Action of Allylic Iodide upon Phenol in the presence of Zinc or Aluminium-Foil.*

By Percy F. Frankland, Ph.D., B.Sc., and T. Turner, F.C.S.

In attempting the synthesis of anethol from allylic iodide and phenol, we had occasion to try the action of these substances upon one another in the presence of zinc and aluminium-foil.

500 grams of phenol were placed in a capacious flask fitted with an inverted condenser, some pieces of zinc and aluminium-foil were also introduced into the flask, and, after gently heating on a sand-bath, 500 grams of allylic iodide were slowly added by means of a dropping-funnel. A violent action, accompanied by evolution of large quantities of hydriodic acid and separation of free iodine, soon set in. When the action had ceased a dark coloured oily liquid, together with

free iodine, remained in the flask. This was washed with ammonia, and then distilled in a current of steam, the retort containing the liquid being simultaneously heated. An oily straw-coloured liquid collected upon the surface of the water in the distillate; this was separated, dried, and repeatedly fractioned. Besides water, there were obtained a fraction passing over between 185 and 195° C. containing unaltered phenol, and secondly, a fraction passing over between 222° and 226° C. The latter, on rectification, passed over between 223° and 225° C.; it was a clear colourless liquid becoming straw-coloured on keeping, and possessing an odour very similar to that of phenol.

On analysis the following results were obtained:—

I. 0·1775 gram yielded 0·5149 gram CO_2 and 0·1393 gram H_2O.
II. 0·1749 „ 0·5074 „ 0·1390 „

The percentage numbers obtained from the above correspond very closely with propyl phenol, whilst they do not agree with those of allyl phenol:—

			Found.	
	Allyl phenol.	Propyl phenol.	I.	II.
C	80·59	79·41	79·11	79·12
H	7·46	8·82	8·72	8·83
O	11·95	11·77	12·17	12·05
	100·00	100·00	100·00	100·00

The boiling point, 223—225° C., also corresponds to that of ortho-propyl phenol, which is given by Spica as 224·6—225·6° C. (corrected) (*Ber.*, **12**, 295). It would thus appear that the allyl phenol, which is probably formed in the first instance, is converted into normal propyl phenol by the hydriodic acid which is liberated in the reaction:—

$$C_3H_5I + C_6H_5(OH) = HI + C_6H_4(OH)(C_3H_5).$$
$$C_6H_4(OH)(C_3H_5) + 2HI = I_2 + C_6H_4(OH)(C_3H_7).$$

LI.—*On a Bye-product of the Manufacture of Aurin.*

By Alexandre Claparède and Watson Smith.

It has been observed that when aurin is prepared from phenol, oxalic acid and sulphuric acid, a relatively considerable quantity of white crystals is formed by sublimation. These crystals appear on the lids of the aurin-pots, as well as in the interior of the vessels used in pre-

paring the colouring matter on the small scale, but their nature has not yet been ascertained. Brought into contact with concentrated sulphuric acid these crystals give a pink colour, turning yellow on addition of water, and red with an excess of alkali, so that there was no possibility of taking them merely for oxalic acid, which they were often believed to be. The product was undoubtedly a compound of oxalic acid with phenol, which it seemed interesting to investigate, and the more so, as it might perhaps throw some light on the process of the formation of aurin. Mr. Charles Lowe, of Manchester, was kind enough to place at our disposal a large quantity of the substance, but its want of stability rendered any process of purification very difficult.

Normal phenyl oxalate, $\begin{vmatrix} COOC_6H_5 \\ COOC_6H_5 \end{vmatrix}$, is known; it has been recently obtained by Nencki (*J. pr. Chem.* [2], **25**, 280) by the action of phosphorous oxychloride on a mixture of phenol and oxalic acid; it melts at 130°, and differs completely in its properties from the substance in question. It is insoluble in water, and can be crystallised from alcohol; whilst the aurin crystals begin to melt at 123°, and are decomposed both by water and by alcohol, with liberation of phenol.

Acid phenyl oxalate, $\begin{vmatrix} COOC_6H_5 \\ COOH \end{vmatrix}$, has not yet been prepared, and it was consequently natural to think at first that the substance might have this composition, but the instability of the bye-product in question made this conclusion unlikely.

Our analyses have shown us that the body is not a real oxalate, but a molecular compound, having the formula—

$$C_2H_2O_4 + 2C_6H_5OH.$$

The substance, as obtained in the preparation of aurin, contained a certain amount of impurity, from which it could not be separated by solution and filtration, owing to its decomposibility in presence of water, alcohol, and ether. Neither has it been found possible to obtain a pure product from the crystals by sublimation. They distil between 150° and 180°, but not without partial decomposition (even under diminished pressure) with formation of formic acid and liberation of phenol. We therefore distilled the crude product, and the distillate which crystallises readily on cooling, after draining well, had to be washed with petroleum spirit, in order to remove the formic acid and free phenol.

The crystals then obtained consist of white, thin, shining plates, giving the following analytical numbers :—

	Substance. grm.	CO_2.	H_2O.
I.	0·2803 gave	0·6130	0·1305
II.	0·2210 „	0·4783	0·1060

	Found. I.	Found. II.	Calculated for $C_{14}H_{14}O_6$.
C	59·7	59·03 per cent.	60·4 per cent.
H	5·17	5·29 „	5·0 „

The phenyl oxalates would require—

	Normal.	Acid.
C	69·42 per cent.	57·83 per cent.
H	4·13 „	3·61 „

It will be found that the percentages obtained for carbon are somewhat too low. This is accounted for by an unavoidable slight decomposition of the substance, with partial loss of phenol. The pure substance, as seen above, has the formula $C_2H_2O_4 + 2C_6H_5OH$, which corresponds with that of crystallised oxalic acid, usually formulated $C_2H_2O_4 + 2H_2O$. As the latter might be considered as the true ortho-oxalic acid, $\begin{vmatrix} C(OH)_3 \\ C(OH)_3 \end{vmatrix}$, the above molecular compound can be considered as a phenyl ortho-oxalic ether—

$$\begin{vmatrix} C_6H_5O.C(OH)_2 \\ C_6H_5O.C(OH)_2 \end{vmatrix},$$

which formula is quite compatible with the unstable nature of the substance.

It melts at 123—124°, boils, with partial decomposition, between 150—180°, is soluble in water, but decomposes almost immediately into oxalic acid and phenol. Alcohol likewise decomposes it, phenol and ethyl oxalate being formed. With ether, disruption occurs, the phenol remaining in solution and crystals of oxalic acid separating. Glacial acetic acid dissolves the substance, and on cooling, beautiful crystalline plates are deposited, which, on exposure, soon lose their lustre, and become white and opaque.

According to the formula, it seemed possible that the substance could be formed from phenol and oxalic acid without the use of a dehydrating agent, and this has been confirmed by experiment. If phenol and anhydrous oxalic acid are mixed in equivalent proportions and distilled together, they also give a good yield of the white crystals melting at 123° to 124°. These were purified in the manner already described, and after drying over caustic potash gave the following results on analysis:—

	Substance. grm.		CO_2.		H_2O.		Per cent. C.	Per cent. H.
I.	0·1770	gave	0·3815	and	0·0810	=	58·8	5·0
II.	0·2190	,,	0·4720	,,	0·1048	=	58·77	5·32

Another method of preparation consists in dissolving phenol and anhydrous oxalic acid in glacial acetic acid. An excess of phenol is to be recommended, in order to avoid the presence of free oxalic acid in the crystallised product. The excess of phenol must then be washed out with petroleum spirit.

Advantage was taken of the instability of the body, to determine the loss of phenol sustained by a weighed portion on heating to a temperature of from 80° to 90°, in a tube closed at one end, until the weight was constant.

The anhydrous oxalic acid thus left amounted to 33·1 per cent., the theoretical number being 32·37.

It will now be interesting to inquire whether this substance plays any intermediate part in the formation of aurin. As is well known to manufacturers of aurin, dehydrated oxalic acid is mixed in the first stage of the process with phenol-sulphonic acid, and it is during this first stage, when the above mixture is gently warmed, that the phenyl ortho-oxalate begins to sublime. This then continues throughout the process. The question now arises, "How has the sulphonic group SO_3H, been removed from the phenol-sulphonic acid, in order to the subsequent formation of the sublimate in question?" This can be explained only by the assumption that on gently heating, oxalic acid unites with the phenol, while simultaneously the sulphonic groups are again separated. This becomes visible in the following scheme:—

$$\begin{matrix} HO.C:O \\ | \\ HO.C:O \end{matrix} + \begin{matrix} HO—C_6H_4—SO_3H \\ HO—C_6H_4—SO_3H \end{matrix} + H_2O = \begin{matrix} (HO)_2C.OC_6H_5 \\ | \\ (HO)_2C.OC_6H_5 \end{matrix} + 2SO_4H_2.$$

The further formation of aurin would then proceed in consequence of elimination of water and formic acid, due to the action of the sulphuric acid:—

$$\begin{matrix} C_6H_5O.C(OH)_2 \\ | \\ C_6H_5O.C(OH)_2 \end{matrix} + C_6H_5.OH = \begin{matrix} C_6H_4.OH \\ C<C_6H_4.OH \\ C_6H_4.O \end{matrix} + HCO.OH + 2H_2O.$$

The phenol taking part in the latter reaction must be derived from a simultaneous decomposition of a portion of the ortho-oxalic ether. The two reactions may be considered to take place at the same time, and therefore the entire formation of the ortho-oxalic ether in the making

of aurin, is not a necessary assumption, but its presence as a sublimed bye-product simply bears witness to the tendency of the first phase of the reaction, which is to the formation of this substance, some of which has escaped the second phase. The first phase can then only be considered as a passing-reaction. The two phases thus shade one into the other, so as to form the full complex reaction.

It is a circumstance worthy of note that the temperature at which the phenyl-oxalic ether melts, and above which it steadily decomposes, is also the maximum limit of temperature to be employed in the method of aurin manufacture, found by experience to yield the best results. Hence this connection of circumstances would seem to bear reasonable witness to the truth of the theory we advance. In any case, pure aurin never having been directly prepared, it is certain that the formation of corallin is not limited to the two phases of the above reaction.

We hope that this research may not be without interest as a contribution to the study of the aurin question.

LII.—*On Samarium and its Compounds.*

By Prof. P. T. Cleve, Hon. Member of the Chemical Society.

Introduction.

In the year 1878 Delafontaine found, on examining impure didymia, extracted from samarskite, some new absorption-bands, which did not belong to didymium but to an unknown element of higher atomic weight. He named this metal *Decipium*. Some time later Lecoq de Boisbaudran found also in the fractions, rich in didymia, which were extracted from samarskite, a new oxide, distinguished by its absorption-spectrum and by peculiar spark-lines. The oxide was thrown down with ammonia before that of didymium. He called the metallic radical *Samarium*, and described more exactly than Delafontaine its absorption-spectrum. In March, 1880, Delafontaine published in the *Bibliothèque universelle de Genève* a paper "On the Atomic Weight and the Compounds of Decipium." The atomic weight was found to be 114, if the oxide be RO (= 171 if R_2O_3). The salts were colourless and the sulphate less soluble than the sulphate of didymium. Shortly afterwards Marignac published his researches on the earths which in the samarskite accompany terbia, and found an oxide, named $Y\beta$, distinguished by its yellow salts, its spectrum of absorption agree-

ing with that of samarium. The atomic weight of the metal was found, as a maximum 99·6, if the oxide be RO (= 179·4 if R_2O_3), thus differing widely from the figures given by Delafontaine. The latter has more recently found that the decipia of 1878 could be split up into an oxide without absorption-spectrum, for whose radical, of the atomic weight 117 (or 171 if R_2O_3) he reserved the name of decipium, and another oxide with the spectrum described by Lecoq de Boisbaudran. He adopted the name of samarium for the metal which has as a maximum the atomic weight 101 (or 151·5 if R_2O_3).

Method of Extraction.

The raw material, which I used for extracting the oxide of samarium, consisted principally of a mixture of almost all the rare oxides of the earth-metals, which were obtained from Dr. Paijkull, in Stockholm, and said to be derived from orthite found at Arendal in Norway. As the matter, about 10 kilos., contained almost 10—12 per cent. thorina, it may be assumed that a considerable quantity of thorite may have been mistaken for orthite. The mixture of earths was mixed with nitric acid and heated in china basins till it began to give off red vapours. After cooling, the mass was treated with water, which left undissolved a large quantity of basic nitrates, principally of cerium and thorium. These basic nitrates were insoluble in saline liquids, but dissolved in pure water, forming opalescent solutions. They were separated by decantation and filtering, and washed as long as the liquid went clear through the filter. The basic salts were mixed with strong sulphuric acid, and the solution of the sulphates in cold water was precipitated with large quantities of hot water, by which operation most of the cerium was separated as basic sulphate.

The solution was then precipitated with caustic soda and the hydrate, principally of thorium, dissolved in diluted sulphuric acid. On evaporating off the solution, large and bulky masses of thorium sulphate were obtained. The oxides, which remained in the mother-liquors, were transformed into nitrates and added to the solution of nitrates obtained by the first operation. These nitrates were evaporated, and the residuum was heated in platinum basins till it began to give off red vapours. On treating the heated mass with water, a solution free from cerium and thorium was obtained.

By this treatment also considerable quantities of the nitrates of the more positive metals, yttrium, didymium, &c., were decomposed, and separated together with the thorium and cerium, and to complete the separation, the basic nitrates were once again and carefully treated in the same manner. The solutions free from the oxides of cerium and thorium, or containing only small traces of these oxides, were

precipitated with potassium sulphate with the view of separating the cerium- and yttrium-oxides, of which the former were (incompletely) precipitated, and the latter (incompletely) retained in the solution.

The yttria earths (about 700 grams) were transformed into nitrates and subjected to the usual melting-process, for separation of erbia from yttria, terbia, and didymia, which offer greater resistance to the action of heat. From the basic nitrates first obtained a small quantity (about 1·5 gram) of scandium oxide was separated.)* They contained also a very small quantity of thulium, some erbia and ytterbia, and a considerable portion of holmia. The fractions containing yttria and didymia were saturated with potassium sulphate, and this precipitate was added to the similar precipitate formerly obtained. These difficultly soluble double sulphates were decomposed with boiling potash-ley, and the hydrates dissolved in diluted sulphuric acid were again treated with potassium sulphate. In the solution there then remained considerable quantities of terbia (about 200 grams impure earth). The precipitate was converted into nitrate and its solution evaporated. The residue was then heated to partial decomposition in order to separate the last remaining traces of thorium and cerium.

The soluble nitrates thus obtained, which contained principally didymium and lanthanum, but also samarium, terbium, yttrium, &c., were mixed with impure didymium, extracted from various minerals as cerite, gadolinite, keilhauite, &c., and then subjected to partial precipitation with cold dilute ammonia. The last fractions contained much lanthanum, which was separated partly by the Mosander method, and partly by precipitation with ammonia. No oxide intermediate between that of lanthanum and that of didymium could be obtained, although I sacrificed much time in searching for such an oxide. The first precipitations were repeatedly treated in the same manner with dilute ammonia. In this way I obtained several fractions containing both terbia and didymia (samarium, &c.). They were again treated several times with sulphate of potash.

The slightly soluble double sulphates were now decomposed, and the solution of the hydrates in nitric acid was repeatedly precipitated with ammonia. I obtained finally the following fractions :—

1 : about 67 grams light-coloured oxides, whose solution was very little coloured, but showed, besides the spectrum of samarium, also the spectrum of didymium. Atomic weight R‴ = 149—150.

2 : about	4	grams	oxide;	at. w. R = 148
3 :	1·7	„	„	= 146·2
4 :	6	„	„	= 143·7

* No scandium could be obtained from the precipitate with sulphate of potassium.

5 : about 150 grams oxide; at. w. R = 142·7
6 : 29 „ „ = 142·3

The sixth fraction was subjected to partial precipitation with ammonia, but the atomic weight of the four fractions thus obtained was still found to be 142·3.

This is a proof of the correctness of my latest determinations of the atomic weight of didymium, which gave the same numbers. No lanthanum was present in these fractions. As the fractions intermediate between the pure or almost pure didymium and the samarium are only trifling, there is very little probability of finding any unknown element intermediate between samarium and didymium.

The 67 grams of earths containing the principal quantity of samarium were now subjected to the same treatment with dilute ammonia, until the absorption-spectrum of didymium was completely eliminated. The oxides freed from didymium were far from pure samarium oxide, and I was therefore obliged to precipitate their solutions with potassium sulphate.

At first I several times used solutions with 2 per cent. oxide, and later with only $\frac{1}{2}$ per cent. Terbia and other oxides (Yα, decipium) were thus eliminated together with much samarium oxide. The treatment with potassium sulphate was continued until the oxide, which remained in the solution, had the same molecular weight as the oxide thrown down, or $R''' = 150$.

A considerable quantity of samaria was separated at the same time as terbia and Yα, for which reason I was obliged to subject these oxides to the same treatment, whereby I finally obtained the fractions used for the atomic weight determinations A and B, A being oxide left in the solution, and B precipitated as double sulphate.

I have described this method, as long experience has convinced me that the coarse separation of all the rare earths may be most conveniently effected thereby.

Atomic Weight of Samarium.

The samarium oxide, obtained as above described, was purified by treatment with sulphuretted hydrogen, repeated precipitation of the solution with ammonia, and finally in acid solution with pure oxalic acid. The oxide obtained by calcination of the oxalate was dissolved in pure nitric acid, and by precipitation with freshly distilled ammonia, divided into four fractions, I, II, III, IV. These were transformed into oxalate and oxide. The four fractions thus obtained were subjected to atomic weight determinations in the usual way, by solution in nitric acid, addition of sulphuric acid, and estimation of the sulphates. The fractions A and B were obtained, as stated in the fore-

going section, from the samarium oxide which remained in the solution of potassium sulphate.

The atomic weight determinations gave the following results :—

	Oxide Sm_2O_3.	Sulphate.	Per cent. of oxide in the sulphate.	At. w. ($SO_3 = 80$.)
I.	1·6735	2·8278	59·180	149·975
II.	1·9706	3·3301	59·175	149·940
III.	1·1122	1·8787	59·201	150·120
IV.	1·0634	1·7966	59·190	150·045
A.	0·8547	1·4440	59·190	150·045
B.	0·7447	1·2583	59·183	150·000

As a mean of these six closely agreeing experiments, the atomic weight is 150·021, or in round numbers 150. In the calculation I have supposed the oxide to be Sm_2O_3, which follows beyond doubt from its chemical properties, that is from the composition of the chloroplatinate, of the samarium and ammonium sulphate, and of the selenite. Whether samarium gives other oxides besides Sm_2O_3 is a point which I have not yet determined. As to its position in the system of Mendelejeff, I think it may most probably be placed in the 8th group, on the 8th line, where there is a gap for a group of unknown elements.

Spectrum of Samarium.

The salts of samarium are distinguished by a peculiar spectrum, composed of several bands, among which four in the blue part of the spectrum are most characteristic. The absorption-spectrum has been examined by Lecoq de Boisbaudran and by Thalén. The latter used a solution of the nitrate prepared by myself.

Both found about the same bands, viz. :—

	Wave-length according to	
Numbers.	Lecoq de Boisbaudran.	Thalén.
I.	559	556 —559
II.	551—500	501·5—497
III.	489 (indistinct)	—
IV.	486—474	486 —472 strong
V.	464—463	466 —460 strong
VI.	—	445 —437 not strong
VII.	417	418·5—415
VIII.	400·75	409 (limit not visible).

The intensity of the absorption is not very great, so that the absence of these bands in didymium salts cannot be regarded as a sure test for the absence of samarium.

The spark-spectrum of samarium has been examined by Professor Thalén, who will soon publish his results. He has found about 150 lines scattered over the whole spectrum, except the red part. They are all of little intensity. Many among these lines were mapped by him in connection with his examination of the spectrum of didymium in the year 1873 (*Kongl. Svenska Vetensk.-Akad. Handlingar*, t. xii, No. 4). The didymia, which I regarded at that time as pure, was thus a mixture of didymia and samaria, which is also apparent from the atomic weight 147, instead of 142·3.

Compounds of Samarium.

Oxide of Samarium, Sm_2O_3, is a white powder, with a scarcely perceptible yellowish tint. If yellow it contains terbia. It is easily soluble in acids, and gives with them salts whose solutions are intensely yellow. The crystallised salts are topaz-coloured, but in the state of powder they are white, with a yellowish tint.

The *hydroxide* is a gelatinous, white, or indistinctly yellowish precipitate, insoluble in alkalis. It is a stronger basic than yttria, but not so strong as didymia.

Chloride of Samarium, $SmCl_3 + 6H_2O$, crystallises in large tabular crystals, which are deliquescent. Pressed between paper, as were all the following salts, it gave by analysis the following results :—

0·5708 gram gave 0·6647 gram AgCl.

0·7375 gram gave 0·3513 Sm_2O_3, precipitated as oxalate.

In per cent.	Calc.	Found.
Sm	41·15	41·06
Cl	29·22	28·79

Chloroplatinate of Samarium, $SmCl_3,PtCl_4 + 10\frac{1}{2}H_2O$, crystallises over sulphuric acid in orange-coloured prisms, which are deliquescent, and lose at 110° 8·71 per cent. H_2O (4 mols. = 9·20).

0·5775 gram gave 0·3611 gram $Sm_2(SO_4)_3$ + Pt, which left on washing with water 0·1402 gram Pt.

	Calc.	Found.
Pt	24·92	24·22
Pt + $Sm_2 3SO_4$..	62·49	62·53

Platinocyanate of Samarium, $2Sm(CN)_3 + 3Pt(CN)_2 + 18H_2O$, obtained by double decomposition of the barium salt with the sulphate, crystallises in well-developed yellow prisms, which reflect blue light. It is unchangeable in the air, and loses at 110° 16·33 per cent. H_2O (14 mols. = 16·57).

0·6963 gram gave 0·5396 gram $Sm_2 3SO_4$ + Pt, which left by washing with water 0·2694 gram Pt.

	Calc.	Found.
Pt	38·46	38·69
Pt + $Sm_2 3SO_4$..	77·12	77·49

Nitrate of Samarium, $Sm(NO_3)_3 + 6H_2O$, crystallises in easily soluble prisms of pale yellowish colour.

1·0969 gram left by ignition 0·4274 gram Sm_2O_3.

	Calc.	Found.
Sm_2O_3.....	39·19	38·96

Acetate of Samarium, $Sm(C_2H_3O_2)_3 + 4H_2O$, forms short, well-developed prisms, moderately soluble in water.

0·7886 gram lost by 110° 0·1393 gram H_2O, and gave by ignition 0·3444 gram Sm_2O_3.

0·8688 gram lost 0·1546 gram H_2O, and gave 0·3802 gram Sm_2O_3.

	Calc.	Found.
Sm_2O_3 ..	43·61	43·67—43·76
H_2O	18·05	17·66—17·79

Sulphate of Samarium, $Sm_2(SO_4)_3 + 8H_2O$, obtained by evaporating on the water-bath a solution of the nitrate mixed with sulphuric acid, forms well-developed brilliant crystals, much less soluble in water than sulphate of didymium.

0·8966 gram lost by careful heating 0·1763 gram H_2O.

0·8240 gram lost 0·1620 gram H_2O.

Both experiments gave 19·66 per cent. H_2O instead of 19·67.

Selenate of Samarium, $Sm_2(SeO_4)_3 + 8H_2O$, is easily soluble in water, but in other respects resembles the sulphate.

0·9881 gram lost by careful heating over the open fire, 0·1642 gram, and left by heating to white-red, 0·3951 gram Sm_2O_3.

	Calc.	Found.
Sm_2O_3.....	39·86	39·99
H_2O	16·49	16·62

Sulphate of Samarium and Potassium, $2Sm_2(SO_4)_3 + 9K_2SO_4 + 3H_2O$, was slowly deposited as a white powder, when acetate of samarium was added to an excess of sulphate of potassium. It is very little soluble in a saturated solution of sulphate of potash. It is difficult to state in figures the solubility, as it seems to be much dependent on the temperature and the more or less quantity of free acid present. I have generally found that 1 litre of the saturated solution contains about $\frac{1}{2}$ gram of samarium oxide.

1·2545 grams lost by heating 0·0246 gram H_2O (hygroscopic ?). The anhydrous salt was dissolved in water, acidulated with HCl, and precipitated with ammonia. The basic sulphate was again dissolved and precipitated. The solutions were evaporated, and gave 0·7229 gram K_2SO_4. The oxide of samarium, precipitated as oxalate, amounted to 0·3157 gram.

	Calc.	Found.
Sm_2O_3	24·87	25·17
K_2O	30·31	31·00
H_2O	1·93	1·96

I have before analysed a compound of didymium, having the same composition.

Sulphate of Samarium and Ammonium, $Sm_2(NH_4)_2(SO_4)_4 + 8H_2O$, or $Sm_2(SO_4)_3(NH_4)_2SO_4 + 8H_2O$, crystallises from the mixed solutions of the simple sulphates containing excess of ammonium sulphate, in small tabular crystals.

0·7168 gram lost by 110° 0·0935 gram H_2O, and left by heating to white-red, 0·2888 gram Sm_2O_3.

	Calc.	Found.
Sm_2O_3	40·28	40·29
H_2O ($\frac{5}{8}$)	12·50	13·04

Selenite of Samarium, $Sm_2O_3,4SeO_2 + 5H_2O$, was thrown down by addition of selenious acid to the solution of the acetate, as a bulky precipitate, which was very soon transformed into microscopic needles.

0·8312 gram lost by 110° 0·0523 gram H_2O, and gave 0·2935 gram Se, and 0·3233 gram Sm_2O_3, precipitated as oxalate.

0·8910 gram gave 0·0560 H_2O, 0·3175 gram Se, and 0·3465 gram Sm_2O_3.

	Calc.	Found.
Sm_2O_3....	39·46	38·90—38·89
SeO_2	50·34	49·61—50·07
H_2O ($\frac{3}{5}$) ..	6·12	6·29— 6·28

Oxalate of Samarium, $Sm_2(C_2O_4)_3 + 10H_2O$, is a white or pale-yellowish crystalline precipitate. From concentrated solutions it is first thrown down as a viscid, yellowish mass, which soon hardens.

1·0029 gram lost by 110° 0·1516 gram H_2O, and gave by ignition 0·4638 gram Sm_2O_3.

	Calc.	Found.
Sm_2O_3	46·77	46·25
H_2O ($\frac{6}{10}$)	14·52	15·12

The salts of samarium agree closely in composition with the

didymium salts; and of all elements, samarium is most nearly related to didymium, less closely to the yttria metals, the platinocyanates of the latter being wholly different from the samarium salt, which resembles the corresponding salts of cerium, lanthanum, and didymium.

LIII.—*The Rate of Decomposition of Ammonium Nitrate.*

By V. H. Veley, M.A., F.I.C., Christ Church Laboratory, Oxford.

Introductory.

Investigations on the course of chemical change have hitherto been for the most part restricted to reactions occurring between the homogeneous liquids, giving as a resultant either another such liquid, or a solid precipitate, or between two or more gases, with one or more gases as a resultant. Among instances of the former class of changes may be mentioned those of Berthelot and Menschutkin on etherification, Harcourt and Esson on the reactions between potassium permanganate and oxalic acid, and hydriodic acid on hydrogen peroxide; of Gladstone on the precipitation of strontium sulphate by the addition of a solution of calcium sulphate to one of strontium nitrate; of Ostwald and Pattison Muir on the decomposition by water of solutions of bismuth salts in acids. Of instances of the latter may be mentioned those of Bunsen, Horstmann, and von Meyer on the combustion of various mixtures of carbon monoxide and hydrogen with oxygen, or nitrous oxide. It seemed interesting to investigate a chemical change in which a gas or mixture of gases is given off from a homogeneous liquid with a view of determining the particular conditions on which the rate of change depends.

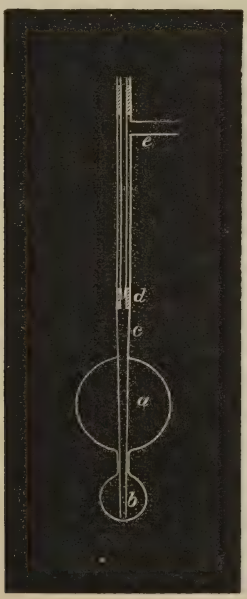
The decomposition of ammonium nitrate seem to offer a case in point, as forming, when melted, a perfectly homogeneous liquid, and giving rise by its decomposition to the production of two gases, nitrous oxide and steam, the latter of which can be condensed into water, while the former can be collected by a suitable apparatus, the rate at which it is given off from a known mass of the salt being taken as the measure of the rate of its decomposition.

The Apparatus used.

In some of the earlier experiments the bulb holding ammonium nitrate was heated to the desired temperature in an air-bath, but it

was found that the temperature could be maintained more constantly by the use of an oil-bath. In both cases the temperature was kept constant by the help of a gas regulator, differing in some respects from others which have been proposed. As the regulator served to keep the temperature of the oil-bath at any point from 250° downwards within a few tenths of a degree, it may be worth while briefly to describe it:—The regulator (Fig. 1) consists of a larger bulb (*a*) filled with olive oil, beneath which is a smaller bulb filled with mercury (*b*). The tube (*c*) to the outside of which the neck of the upper bulb is fastened, is drawn out below to a small tapered tube which passes through the contraction, where the bulb joins, to the bottom of the lower bulb. Expansion of the oil by heat causes it to descend into the lower bulb, while mercury rises in the stem of the instrument. A copper tube tapering at the end to an opening of about 2 mm. diameter, and surrounded at the point by a stout closely fitting copper collar (*d*) works within the glass stem, thus leaving only sufficient space for the return of the gas which enters by the copper tube. This collar is about 5 mm. in height, and projects 2 mm. beneath the orifice of the copper tube. The gas leaves the stem by a lateral tube (*e*) near the top. The position of the copper tube which determines the temperature, for which the regulator is set, is adjusted by sliding

Fig. 1.—Mercury and Oil Gas Regulator.



it up or down through a gas-tight stuffing box through which it moves with sufficient friction to maintain its position. Olive oil has a high rate of expansion, and is unchanged by a temperature of 250°. By giving the stem a diameter of about one-eighth of that of the larger bulb an increase from the ordinary temperature up to 280° will cause the mercury to rise about a decimeter. When the rising mercury meets the copper collar it is enclosed within a comparatively narrow tube, and a small change of temperature causes then a greatly magnified change of level. After a time the convex surface of the mercury sets itself at such height beneath the central tube, that just so much gas is admitted as serves to maintain the temperature. The pressure of the gas should be kept constant by passing it through an ordinary governor on its way to the regulator.

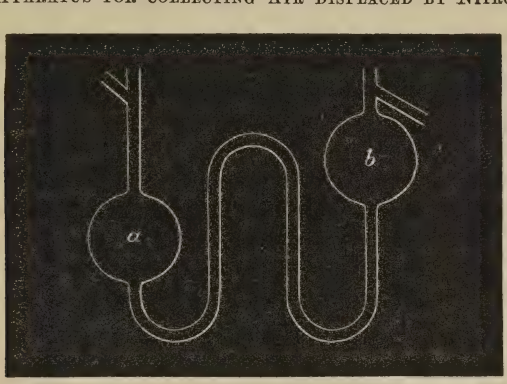
The apparatus for observing the rate at which gas was evolved from the ammonium nitrate consisted of two inverted **U**-tubes of the same capacity and calibre, having two limbs, one of each in close contact, and wired together above and below. In the centre of the upper horizontal part of one of these tubes is fixed a stop-cock, through which, by means of a piece of flexible tubing, water can be drawn up till the tube is filled, when the open ends are standing in a pneumatic trough. In this tube the gas is collected, rising in bubbles through one limb, while in the other limb the unbroken surface of the water falls steadily. The second tube contains a measured quantity of air, the level of the water in one limb serving to mark the point where an equal volume of gas has been collected in the twin **U**-tube, the level of the water in the two adjoining tubes being at that moment the same. The actual volume and level varies with temperature and atmospheric pressure; but since the contents of the two tubes are under the same conditions this variation is immaterial. The volume of air used as a measure in these experiments was equal to the volume of nitrous oxide produced by the decomposition of 0·05 gram of ammonium nitrate.

The apparatus which has been described was used in some earlier experiments in which nitrogen and nitric oxide were the gases evolved. The insolubility of water in these gases made it possible to collect them directly in the **U**-tube, passing the volume that was evolved between each observation of equality of level and the refilling of the tube into a small separate tube from which it could be decanted into the **U**-tube during the time of the next observation. Unfortunately with nitrous oxide this method of continuous observation was not available, and some complication was necessary since the solubility of the gas in water would have affected the intervals in which equal volumes were collected.

The plan adopted was to interpose a bent tube provided with two

bulbs, *a* and *b* (Fig. 2), and charged with a solution of potassium sulphate between the generating flask and the **U**-tube. At both ends of the bent tube was a second outlet opening into the air. The bottom of the bulb, *b*, connected with the delivery-tube was on a level with the top of the bulb, *a*, connected with the generating flask. When both were opened to the air, the upper bulb was empty and the lower filled with the solution. On closing the aperture, the stream of nitrous oxide forced the liqnid down in one bulb and up in the other, driving the air which it displaced into the measuring tube. Nitrous oxide dissolves more sparingly in potassium sulphate solution than in pure water, and the small quantity of the solution which came in contact with the gas was soon saturated, the length of bent tube interposed between the bulbs hindering mixture and diffusion. When an observation had been made, both outlets were opened, and the liquid returning to its level expelled the nitrous oxide from one bulb, and recharged the other with air. Thus each measure of nitrous oxide was represented by the collection in the measuring tube of its own volume of air.

Fig. 2.—Apparatus for collecting Air displaced by Nitrous Oxide.



The observations were made with the help of a clock beating seconds stationed close to the apparatus, by noting and then keeping count of the seconds while watching in which second the water slowly falling in one tube became exactly level with the similar column of water by its side. The beginning of each observation was similarly noted by watching, when counting the seconds, for the first bubble which entered the measuring tube. The interval between the times thus noted was that required for the decomposition under the conditions of the experiment of 0·05 gram of ammonium nitrate.

The time elapsing between two successive observations while the

measuring tube was refilled with water and the bulb recharged in the manner described, was made as short as possible, and has been allowed for in reducing the observed intervals to what they would have been if the mass of ammonium nitrate undergoing decomposition had been constantly 100 grams.

The Melting Point and Point of Decomposition of the Salt.

Observations on the temperature at which ammonium nitrate melts and enters into decomposition differ very widely; in the more modern text-books and dictionaries it is stated that the salt melts at 108°, and begins to decompose at about 280°. Pickering (this Journal, 1879; Abstr., 200), however, gives 165° and 185° as the points in question. In order to ascertain these points, a thin glass tube was blown out into a bulb which was filled with a sufficient quantity of the dried salt to completely cover a considerable length of the stem of a thermometer enclosed within the bulb. The bulb was heated in a bath of glycerin kept constantly stirred. The salt first showed signs of fusion at 150° C., and melted with a clear transparent liquid at 159° (mean of three concordant results), under a barometric pressure of 753 mm., at which point it could be kept for an indefinite period in a perfectly liquid state. The discrepancy between former observations and those of Pickering and the author doubtless arises from the fact that the salt passes, like the caustic alkalis, immediately from a state of solution to that of fusion. With the same apparatus it was found that a distinct evolution of the mixed gases begins at 186°, and in the course of experiments with the apparatus described above, observations were made at 190°. The melting point and point of decomposition were unaltered by reducing the pressure to 10 mm. by a Sprengel pump.

Purification of Salt.

In order to purify the salt it was dissolved in water, and the solution, after filtration, was evaporated down with about 5 c.c. concentrated nitric acid in order to oxidise and destroy organic substances, especially compound amines derived from the coal-gas ammoniacal liquors from which the salt was doubtless originally prepared. The fused salt, obtained from the evaporation, was kept in a desiccator over sticks of potash until required for use. In some cases the salt was submitted to a further process of purification by being kept for several hours at a temperature slightly above its melting point. The salt used throughout the experiments was free from ammonium chloride and sulphate.

Details of Experiment.

About 100 grams of the salt were weighed and quickly melted in the decomposition flask before the introduction of the latter into the oil- or air-bath. At the close of each experiment, the flask containing the salt was cooled as rapidly as possible and weighed, in order to ascertain the mass of salt which had disappeared in the course of the decomposition. To render the observations comparable, the results were reduced on the supposition that a constant mass of 100 grams was present in the flask.

Preliminary Observations

showed that the rate of change decreased in a proportion greater than that corresponding to a diminution in mass, while the reaction of the salt became decidedly acid from the presence of free nitric acid. (In order to decide whether the acid present was nitric, nitrous, or hyponitrous acid, a large quantity of the salt from one of the series of experiments was dissolved in water, and the solution obtained was found to exert no reducing action on acidified potassium permanganate solution, and thus the presence of the two latter acids is precluded.) It has long been known that other ammonium salts after heating possess an acid reaction owing to the partial escape of ammonia; the well-known experiment illustrating the dissociation of ammonium chloride, which consists in introducing a slip of moistened blue litmus-paper into the salt after volatilisation, illustrates the phenomenon. Further former experiments proved that a similar change occurs in the course of the preparation of nitrogen from concentrated solutions of potassium nitrite and ammonium chloride.

SERIES I. TEMPERATURE 210°.

Intervals of Time required for Unit Change in Minutes and Decimals of a Minute.

Constant Mass of Salt = 100 grams.

2·10	2·20	2·30	2·35	2·35	2·40	2·6	2·75	2·75	2·85	3·0
2·10	2·25	2·30	2·35	2·35	2·55	2·6	2·80	2·75	2·90	3·1
2·15	2·25	2·35	2·35	2·40	2·60	2·7	2·75	2·75	2·95	3·1

With a view of preventing the formation of acid, and of obtaining constant results, a fragment of litharge was dissolved in the fused salt; the effect of the presence of free ammonia from the decomposition of a portion of the salt by the oxide was to raise the temperature at which the salt gave off nitrous oxide; the salt was heated for 45 minutes at 220°, without evolution of gas other than ammonia.

The decomposition set in at 223°, and the rate of change increased gradually until it finally became too fast for observation.

Series II. Temperature 223°.

Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

71·00	20·35	8·00	3·35	1·6
43·65	14·60	5·95	2·55	1·3
29·40	10·80	4·50	2·00	1·1

In order further to investigate the effect of the presence of ammonia, this gas was passed into the fused salt when in a state of fusion, until a small test portion when removed, and dissolved in water, gave a solution possessing a faint alkaline reaction. The salt was then heated for some time at 220—230°, in order to drive off the greater part of the free ammonia; then the temperature was lowered to 210°.

Series III. Temperature 210°.

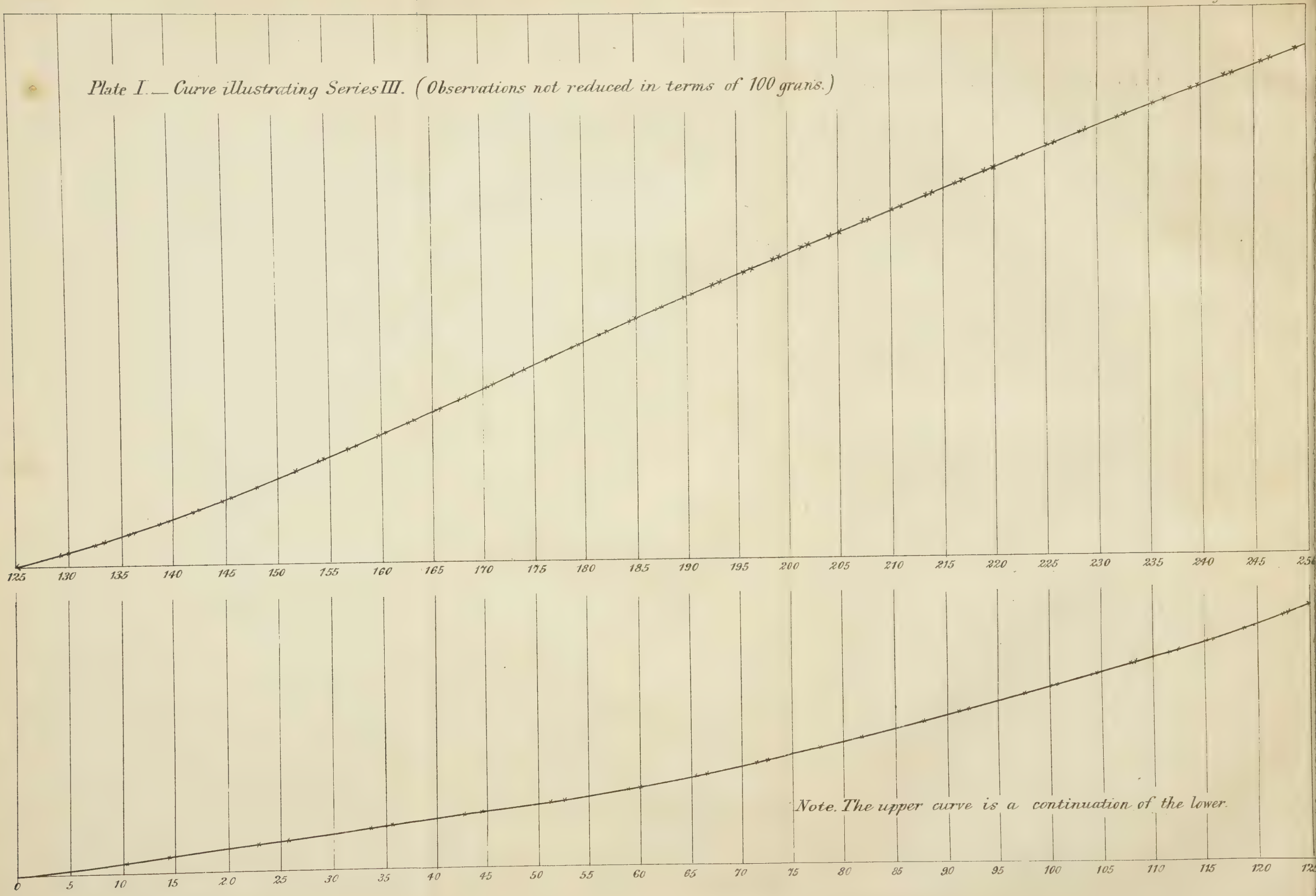
Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

24·90	8·20	3·95	3·00	2·50	2·50	2·70	3·10	3·5
22·60	7·60	3·90	2·75	2·50	2·55	2·70	3·15	3·5
20·20	6·55	3·70	2·65	2·45	2·55	2·70	3·15	3·5
16·60	5·85	3·55	2·45	2·45	2·60	2·75	3·15	—
14·30	5·30	3·40	2·55	2·45	2·60	2·85	3·25	—
12·50	4·80	3·40	2·55	2·45	2·60	3·00	3·35	—
11·25	4·65	3·25	2·45	2·45	2·60	3·00	3·40	—
10·05	4·85	3·10	2·50	2·45	2·70	3·10	3·50	—
8·90	4·25	2·95	2·50	2·45	2·70	—	—	—

The actual observations are graphically illustrated in Plate I, in which the ordinates represent the units of decomposition, and the abscissæ the time in minutes from the commencement of the experiment; the points at which observations were made are marked by small crosses. The experiment was repeated in the same form with the exception that the salts were heated for a short time at 240°, in order to accelerate the giving off of the ammonia.

Plate I.—Curve illustrating Series III. (Observations not reduced in terms of 100 grains.)



Harrison & Sons. Lith. St. Martins Lane W.C.

Plate II. Curve illustrating Series VI. (Observations not reduced in terms of 100 grans).

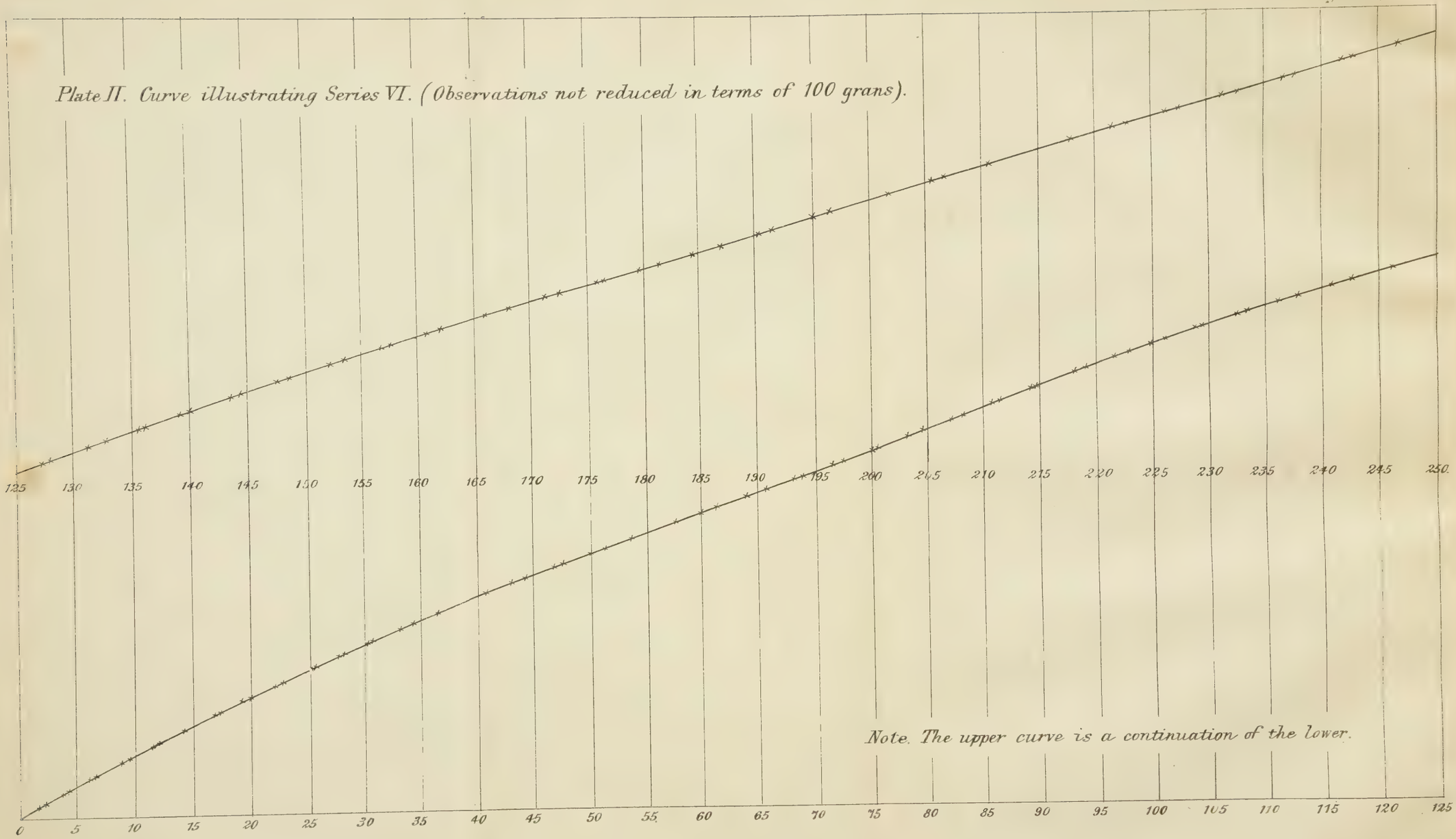


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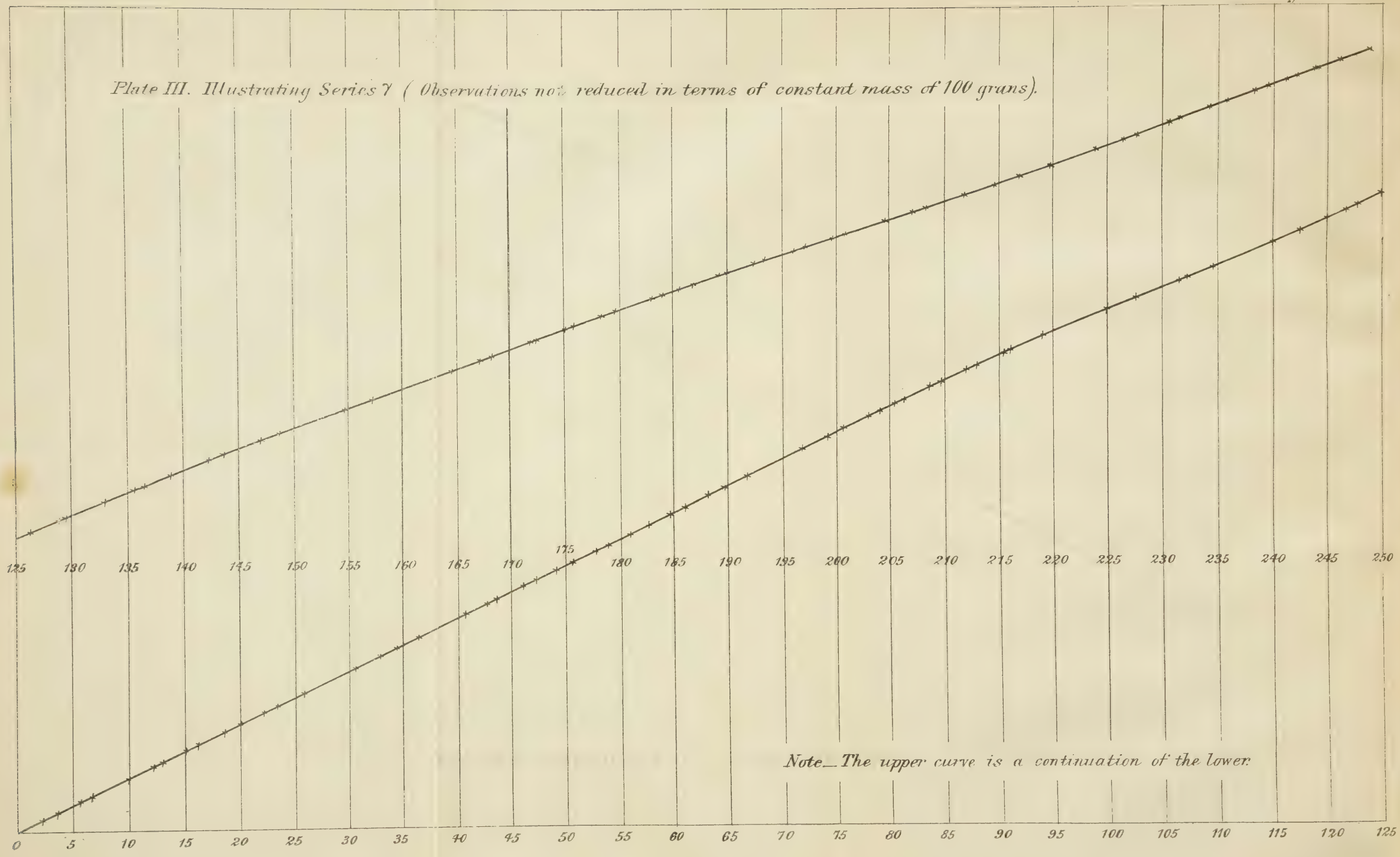
Plate III. Illustrating Series γ (Observations not reduced in terms of constant mass of 100 grams).



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SERIES IV.

Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

3·3	2·6	2·4	2·6	2·6	2·6	2·7	3·20
3·2	2·6	2·4	2·6	2·6	2·6	2·8	3·25
3·1	2·5	2·4	2·6	2·6	2·6	2·9	3·25
3·1	2·5	2·5	2·6	2·6	2·6	3·0	3·25
3·1	2·4	2·5	2·6	2·6	2·6	3·0	3·35
3·1	2·4	2·5	2·6	2·6	2·6	3·0	3·35
2·9	2·4	2·5	2·6	2·6	2·6	3·0	—
2·9	2·4	2·5	2·6	2·6	2·7	3·1	—

In the two series of experiments above, the decomposition proceeds in the same course; the ratio at first gradually increases until a point of maximum velocity is reached, at which it remains constant for some time; after passing through this stage the rates decrease more slowly. These variations are graphically illustrated by Plate I, the curve at first is flat, and becomes gradually steeper until it is practically a straight line, from this point it again becomes flatter, and if the experiment were continued long enough it would probably attain its former degree of flatness. These experiments were repeated several times, and the chemical change followed invariably the same course.

In order further to study the effect of the ammonia, a strong solution of it was warmed gently, and the gas delivered into the molten salt through a finely drawn out tube, and the flow of gas regulated at will. Experiments proved that the decomposition could be stopped completely by the ammonia, even at very high temperatures.

SERIES V.

Temperature.	Intervals of time required for unit change.	Remarks.
210°	4·70	
	4·95	
	5·95	Current of ammonia increased.
	7·42	
	Decomposition stopped.	
230°	4·10	
	2·55	
	2·10	
	2·70	Current of ammonia increased.
	17·60	Ditto.
	Decomposition stopped.	
240°	2·45	
	1·30	
	8·30	Current of ammonia increased.
	Decomposition stopped.	

Note.—The observations in the series above are not reduced in terms of the constant mass of 100 grams.

As it was found exceedingly difficult to regulate the current of the ammonia so as to obtain a constant rate of change, a more prolonged series of observations were made with the salt, previously acidified by evaporation with concentrated nitric acid, in order to trace out the various phases of the change.

SERIES VI. TEMPERATURE 210°.

Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

1·85	2·30	2·70	3·00	3·50	3·90	4·30	4·55
2·00	2·35	2·80	3·00	3·55	3·90	4·30	4·55
2·00	2·35	2·75	3·05	3·60	4·10	4·30	4·65
2·05	2·40	2·85	3·10	3·65	4·10	4·30	4·65
2·10	2·40	2·90	3·20	3·70	4·15	4·30	4·70
2·10	2·55	2·95	3·35	3·80	4·10	4·30	4·75
2·15	2·60	2·95	3·35	3·80	4·10	4·35	4·75
2·15	2·65	3·00	3·40	3·80	4·10	4·45*	4·75
2·25	2·70	3·05	3·45	3·90	4·20	4·45	—

In this series there is a gradual decrease of rate, with a tendency towards constancy at the conclusion. The actual observations to the point marked are graphically illustrated in Plate II.

As a confirmation of the results a more protracted series of experiments were undertaken, the course of the decomposition being observed continuously for nearly 12 hours.

SERIES VII. TEMPERATURE 210°.

Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

2·25	2·55	2·90	3·50	4·05	4·30	4·70	5·20	5·40
2·25	2·55	2·95	3·55	4·05	4·35	4·75	5·25	5·40
2·25	2·55	3·00	3·60	4·10	4·40	4·85	5·30	5·40
2·25	2·60	3·05	3·60	4·10	4·50	4·85	5·30	5·45
2·30	2·65	3·10	3·60	4·15	4·50	4·90	5·30	5·45
2·35	2·70	3·05	3·65	4·15	4·55	5·05	5·30	5·45
2·30	2·75	3·10	3·70	4·15	4·60	5·00	5·35	5·45
2·40	2·75	3·25	3·65	4·15	4·50	5·00	5·35	5·45
2·40	2·80	3·25	3·80	4·20	4·50	5·00	5·40	5·50
2·40	2·75	3·30	3·85	4·30	4·55	5·00	5·40	—
2·45	2·80	3·40	3·95	4·20	4·55	5·10	5·40	—
2·55	2·85	3·45	4·00	4·20	4·65	5·10	5·40	—

The results here arrived at confirm those in the preceding series,

the tendency towards constancy being more marked at the close of the series, for there is an increase of 0·1 minute only in the last thirteen observations. It was finally found that approximately constant results could be obtained when the salt was heated for several hours, generally from about 7 P.M. to 10 A.M., at 205°, before observations were made; the salt was then heated to the temperature required. Series of experiments were concluded at 220° (viii), 215° (ix), 210° (x).

Series VIII. Temperature 220°.

Loss in Weight before Observations were made = 10 per cent.

Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

2·25	2·25	2·25	2·15	2·15	2·2
2·25	2·25	2·25	2·15	2·20	2·2
2·25	2·25	2·20	2·15	2·20	2·2
2·25	2·25	2·20	2·15	2·20	2·2
2·25	2·25	2·15	2·20	2·20	2·2
2·25	2·25	2·15	2·20	2·20	—
2·25	2·25	2·15	2·20	2·20	—
2·25	2·25	2·15	2·20	2·20	—

The rate of change throughout this series is perfectly constant, the greatest difference between any two observations being 0·1 minute, which lies within the limit of experimental error.

Series IX. Temperature 215°.

Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

2·40	2·40	2·55	2·60	2·70	2·70	2·75	2·80
2·40	2·45	2·55	2·55	2·70	2·75	2·75	2·80
2·35	2·45	2·60	2·65	2·70	2·75	2·75	2·85
2·40	2·50	2·60	2·65	2·70	2·75	2·75	2·85
2·40	2·45	2·60	2·70	2·70	2·75	2·75	2·85
2·40	2·50	2·60	2·65	2·70	2·75	2·75	2·85
2·40	2·50	2·60	2·65	2·70	2·75	2·80	2·80
2·45	2·50	2·60	2·65	2·65	2·70	2·80	2·80

In this series there is a slight increase of rate at first, while it ultimately becomes constant; the extreme variation in the last 32 observations being 0·15 minute, which could be accounted for by the rise or fall in the temperature of about 1°. The course of the change is graphically represented in Plate III.

Series X. Temperature 210°.

Loss in Weight before Experiments were commenced = 9·8 per cent.

Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

6·15	6·3	6·55	6·4	6·5	6·6	6·4
6·15	6·3	6·55	6·5	6·5	6·5	6·5
6·25	6·3	6·45	6·5	6·6	6·5	6·4
6·25	6·4	6·50	6·5	6·6	6·5	6·5

In this series also the rate slowly increases until a constant velocity is reached. The extreme variation in the last 21 observations being 0·2 minute, or less than 3 per cent., a difference, which could easily be accounted for by a very slight change in temperature.

The average numbers in the three preceding series may be taken to be 2·2, 2·8, and 6·5 ; they do not seem to be in any simple logarithmic ratio.

These experiments were also made on a more extended scale, with the salt rendered previously alkaline, by the passing in of ammonia ; test portions were removed from time to time, dissolved in water, and the proportion of acid present determined.

Series XI. Salt Alkaline.

Intervals of Time required for Unit Change.

Constant Mass of Salt = 100 grams.

3·75	2·40	2·25	2·40	2·55	2·75	2·95
3·65	2·40	2·30	2·40	2·55	2·85	2·95
3·50	2·30	2·25	2·40	2·70	2·90	3·05
3·35	2·20	2·35	2·50	2·75	2·95	3·05
3·15	2·25	2·35	2·60	2·75	2·95	3·15
3·15	2·25	2·35	2·65	2·75	2·95	3·25
2·95	2·25	2·40	Sample re-	2·75		Sample re-
2·85	2·30		moved, free			moved, free
Sample re-			acid = 0·27 p.c.			acid = 0·2 p.c.
moved, free						
acid = 0·21 p.c.						

The Rate of Change Dependent upon the Proportion of Free Acid Present.

In order to ascertain how far the variation in rate is dependent upon the proportion of free acid present at various periods of the decomposition, a small quantity (about 10 grams) was poured out of the decomposition flask into a weighed basin. It was then allowed

to cool under a desiccator, and the proportion of free acid determined by dissolving the salt in water, and titrating the solution by a solution of ammonia of known strength. Litmus was used as the indicator, and in order to insure greater accuracy, each determination was compared with a solution of standard tint, kept in a closely corked flask.

The first experiments were a repetition of Series III and IV, in which ammonia gas was passed in before the salt was heated to its point of decomposition; observations were made on heating the salt to 210°, until the point of maximum velocity was reached, when test portions were removed and heated as described above.

	Intervals of time required for unit change.	Percentage of free nitric acid.
Series α	2·2	0·27
Series β	2·1	0·31

Experiments were made in repetition of Series VI and VII with the salts previously acidified; during the earlier stages of decomposition the smell of nitric oxide was distinctly perceptible, the gas being doubtless formed by the decomposition of the free nitric acid.

SERIES XII. TEMPERATURE 210°.

Intervals of time required for unit change.	Percentage of free nitric acid.
1·95	0·40
2·91	0·26
4·15	0·17
4·40	0·10

SERIES XIII. TEMPERATURE 210°.

Intervals of time required for unit change.	Percentage of free nitric acid.
1·25	0·66
3·30	0·19
4·35	0·18

A repetition of Series XII.

SERIES XIV. TEMPERATURE 210°.

Intervals of time required for unit change.	Percentage of free nitric acid.
0·60	0·71
2·00	0·41
2·50	0·27

A repetition of Series XII and XIII.

Further experiments were also made to ascertain the condition of the salt, rendered previously alkaline by the passing in of ammonia gas, when appreciable decomposition sets in.

SERIES XV. TEMPERATURE 220°.

Interval of Time required for Unit Change.

Reaction of salt alkaline at commencement.

39·75
15·00

The reaction of the salt at this point was found to be perfectly neutral.

SERIES XVI. TEMPERATURE 225°.

Intervals of Time required for Unit Change.

59·35
30·55
70·75

A repetition of Series XV.

The salt at this point was found to contain a trace (less than 1 in 10,000) of ammonia.

Collecting the results obtained in the series above, together with others made in the course of the investigation, it is evident that the rate of change is greater the greater the proportion of free acid present in the salt.

Intervals of time required for unit change in minutes. Temp. 210°.	Percentage of free nitric acid.
0·60	0 71
1·25	0·66
1·95	0·40
2·00	0·41
2·10	0·35
2·20	0·27
2·50	0·27
2·85	0·21
2·90	0·26
3·25	0·20
3·30	0·19
4·15	0·17
4·35	0·18
4·40	0·10
4·75	0·05
15·00	Nil
17·75	Trace of ammonia

The numbers representing the proportion of free acid are not so accurate as could be desired, but an error in the determination, caused by the addition of a drop too much or too little of the ammonia solution, would account for the irregularities, as the quantity to be estimated is very small.

Conclusions.

I. The rate of decomposition of ammonium nitrate into nitrous oxide and water is dependent not only upon the mass of salt undergoing decomposition, but also upon the proportion of free nitric acid present.

II. If the reaction of the salt be rendered alkaline at starting, the rate of decomposition gradually increases while the proportion of free acid increases; a period of maximum velocity is then reached, corresponding to the greatest proportion of free acid; from this point the rate decreases very slowly, while the proportion of free acid also decreases.

III. An excess of ammonia obtained either by passing in the gas, or by the addition of a basic oxide, will completely stop the reaction, even at temperatures 50—60° above the normal point of its decomposition.

IV. If the reaction of the salt be rendered acid at starting, the rate of decomposition gradually decreases, while the proportion of acid gradually decreases.

V. After heating the salt for about 13—16 hours, the rate of change becomes practically constant.

The author wishes to return his best thanks to Mr. Vernon Harcourt, not only for devising the various parts of the apparatus, but for much valuable assistance and advice during the course of the investigation; and also to acknowledge a grant from the Royal Society in aid of the research.

LIV.—*On Evaporation in Vacuo.*

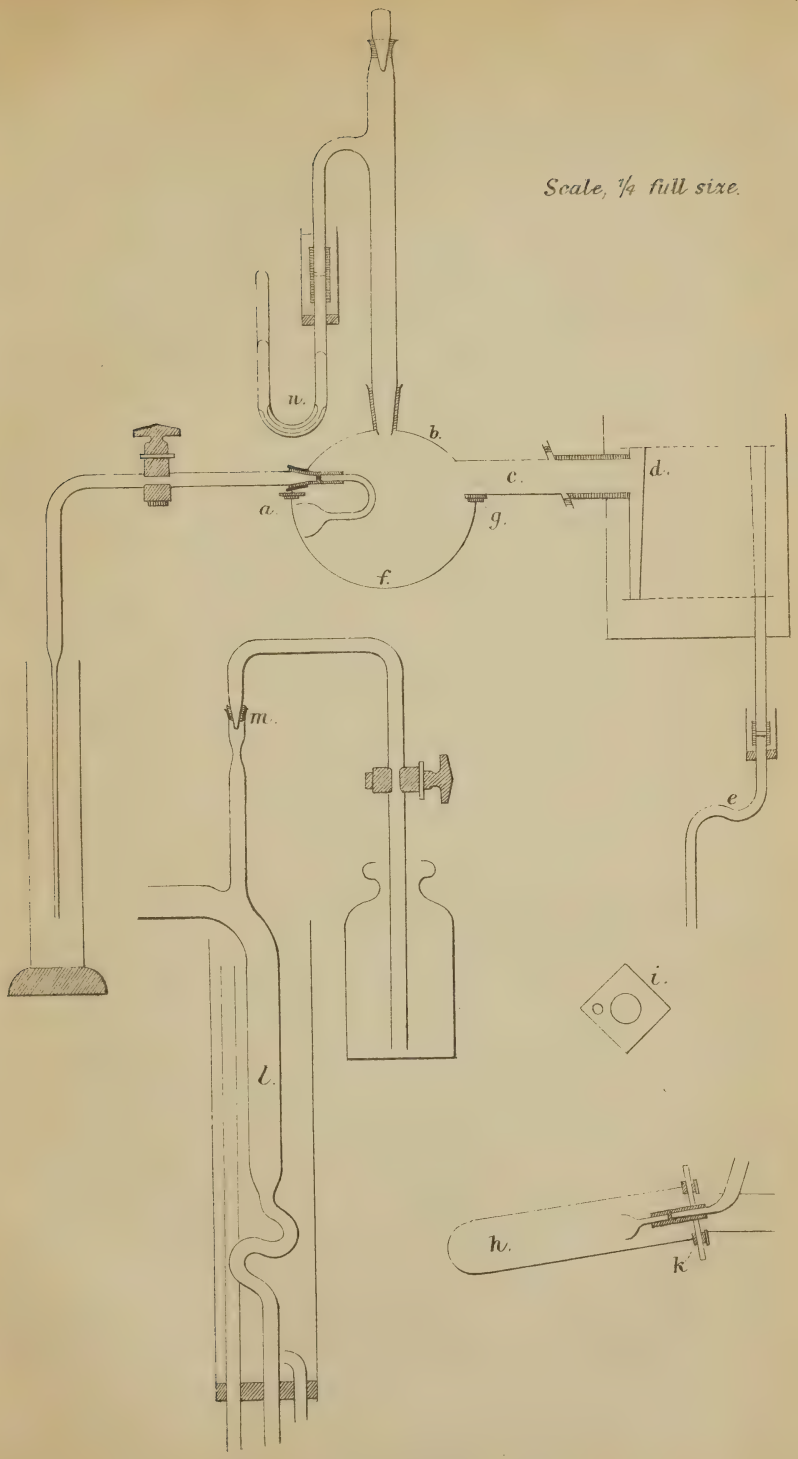
By Herbert McLeod.

The ordinary method of evaporation *in vacuo* by placing the liquid in a dish over sulphuric acid in an air-pump receiver is very slow, and for three reasons: firstly, the aqueous vapour reaches the surface of the acid by diffusion only, for by an ordinary air-pump it is possible only to obtain a considerable rarefaction, and not to remove all the air from the receiver; secondly, the surface of the sulphuric acid is limited, and as the dilute sulphuric acid has a lower density than the oil of vitriol it forms a layer on the surface of the latter, and much retards the absorption; and, lastly, heat is supplied only very slowly to the evaporating liquid, principally by radiation, for not much heat will be carried by convection in a highly attenuated atmosphere. In an experiment tried in order to determine the rate of evaporation under these conditions, 50 c.c. of distilled water placed in the vacuum of a good air-pump over 250 c.c. of sulphuric acid required $2\frac{1}{4}$ days for complete evaporation.

I was led to try some experiments on the evaporation of water at low temperatures by some remarks in Professor J. W. Mallet's paper "On the Determination of Organic Matter in Potable Water" (*Chem. News*, **46**, 62, 73, 90, 101, 108), and the method was suggested by Mr. A. W. Wright's "Apparatus for the Distillation of Mercury *in Vacuo*" (*ibid.*, **44**, 311). When the experiments were nearly concluded, another paper by Professor Mallet appeared in the *Chemical News* (**47**, 218, 252), in which an apparatus is described which bears a very close resemblance to one which I had constructed in the early part of the investigation, and although this seems to have answered all the purposes for which it was designed, it may not be without interest to describe some of the most successful forms at which I have arrived.

In distilling mercury in Wright's apparatus, it is at once obvious that the operation proceeds very much more rapidly and at a much lower temperature, and also without ebullition, when the last traces of air are removed; hence it seemed necessary in the evaporation of water to arrange the apparatus so that the condensed water should itself pump out the gas that is liberated during the evaporation.

One form of the apparatus consists of a horizontal flat brass ring, *a*, 118 mm. in its outside diameter and 92 inside; to the upper side of the ring a dome of copper, *b*, is soldered. The dish containing the water to be evaporated is attached to the lower surface of the brass ring in a manner that will be afterwards described. The dome is pro-



Harrison & Sons, Lith., St Martins Lane, W.C.

vided with a horizontal copper tube, *c*, 18 mm. wide, by which it is connected with a copper condenser, *d*, consisting of a truncated cone within a cylinder, the space between the two being enclosed at the top and bottom by means of copper rings soldered on. This forms a condenser of small capacity and with a large cooling surface; it is fixed in a tin can, through which a stream of water can be made to flow. It is necessary that the connecting tube between the dome and the condenser should be wide, so as to permit of the rapid passage of the rarefied aqueous vapour. The bottom of the condenser is provided with a narrow brass tube, to which is attached a glass tube with a bend, *e*, near its upper end, in which the drops of water are formed which produce the exhaustion. In a laboratory where a fall of about 35 feet is obtainable this might constitute the whole apparatus, but not having at my disposal a greater height than that of the laboratory bench, the lower end of the fall-tube is fitted into the neck of a Woulfe's bottle, which latter is connected with a Körting's jet pump to remove the air at the commencement of the operation. The Woulfe's bottle is also provided with a siphon for the removal of the condensed water.

The dish, *f*, in which the evaporation is performed is an ordinary hemispherical glass evaporating dish about 100 mm. in diameter, and with its edge ground smooth. A wetted red india-rubber ring, *g*, is placed on the lower surface of the brass ring attached to the dome, the edge of the dish being pressed upwards against it, and the jet pump set in action. The atmospheric pressure soon holds the dish firmly in position. The red india-rubber ring is preferable to ordinary sheet india-rubber, as it does not adhere firmly to the glass when the dish has to be removed; it also may be used a large number of times. When the vacuum is as good as the pump will make, a small quantity of distilled water is allowed to flow into the dish from a supply tube provided with a stopcock and attached to a small tubulure on one side of the dome. This supply tube terminates in a small funnel which touches the inside of the dish so that the admitted water flows down the side of the dish in a thin film. The dish is then surrounded by a water-bath heated to 50°. The last traces of air are thus expelled from the dish and condenser, and a current of water is then turned on to the condenser. It is necessary also that the Woulfe's bottle and the fall-tube should be kept cool, and this is best effected by allowing the overflow from the condenser to run down the outside of the fall-tube into a vessel surrounding the bottle. When the vacuum is complete, the water around the condenser is removed, and the water to be evaporated is allowed to flow slowly into the dish. 50 c.c. at a time may be admitted, the water-bath being maintained at 40° or 50°, preferably with the aid of a thermostat. Much of the

dissolved air escapes during the entrance, and, if time can be spared, it is advisable to allow the water to remain in the vacuum for an hour or so to avoid the violent ebullition which sometimes occurs. If it is necessary that the evaporation should be begun at once, it is better to raise the temperature of the water in the bath very slowly from 30° to 50° while the water is running round the condenser. No experiment has been made with water cooled with ice, that of the supply being always employed. Water soon begins to form in the condenser, and the drops flow down the fall-tube and pump out the air. When the air is removed the evaporation proceeds at a rapid rate, and in some cases in which the temperatures were observed, the water was at 26° whilst the temperature of the bath was 50°. Of course the temperature of the evaporating water will depend also on that of the water surrounding the condenser. It is hardly necessary to observe that although the temperature of the water is low, the solid residue is heated to the temperature of the water-bath.

Tumultuous ebullition sometimes takes place, and this is the principal objection to the process. If the water has been previously mixed with sulphurous acid and raised just to the boiling point before introduction into the apparatus, the evaporation proceeds much more quietly, the violent boiling being produced apparently by the escape of carbonic anhydride from the decomposition of acid carbonates. When the water is nearly all evaporated there is considerable effervescence.

The evaporation proceeds at about the rate of 50 c.c. in 2 hours. In an open dish over a water-bath the same quantity of water is evaporated in about 1—1½ hours.

To avoid loss from spirting, the evaporation may be carried on in a wide test-tube (*h*), the condenser being provided with a glass plate (*i*), pierced with two holes, a large one through which the vapour enters the condenser, and a small one through which the supply tube passes into the evaporating tube; an india-rubber ring (*k*) makes an air-tight joint between the plate and the mouth of the tube. The test-tube is very slightly inclined to the horizontal, and is surrounded by a water-bath. The water to be evaporated is allowed to flow in slowly, and the evaporation carried out at the same time. Even if violent boiling takes place, the liquid is only thrown across the tube, and the residue is not lost. This form of apparatus may be useful when the residue is to be determined, and it is not necessary to remove the solid, and it has the further advantage that the tube may be closed during the weighing by a glass cap, which diminishes the rate at which the residue absorbs water from the air.

The evaporation in the tube is slower than in the dish for two reasons: firstly, the evaporating surface is smaller; and secondly, gas

continues to be evolved during the whole process, thus producing an increased pressure. A light spherical flask may be employed in place of the test-tube, and has the advantage of permitting 50 c.c. of the water to be introduced at a time, without danger of loss from ebullition.

When a combustion of the residue is to be made with cupric oxide, by Frankland and Armstrong's process, the evaporation might be performed in the combustion tube itself, and in contact with the oxide of copper. For this purpose one end of the combustion tube is connected to the condenser, and the other end which is drawn out and bent at right angles, is connected with the supply tube, and the tube heated in the water-bath. The increased surface thus obtained much hastens the evaporation. It remains for water analysts to ascertain if the method is practical.

Another modification of the method is to replace the condenser by a wide vertical tube (*l*), along the inner surface of which a thin layer of sulphuric acid is allowed to pass, the acid being admitted by a tubulure (*m*), and regulated by a stopcock. The water vapour is rapidly absorbed, and passes down the fall-tube as dilute sulphuric acid. In this way it is possible to conduct the evaporation at a temperature only a few degrees above the freezing point, the water-bath being maintained between 30° and 40°. By surrounding the wide tube with a flow of cold water, the evaporation is more rapid and the acid is much economised, one volume of water requiring about one of sulphuric acid for its evaporation; if the tube is not cooled about three volumes of acid are necessary.

Care is necessary in regulating the flow of acid, for if too rapid the water may be frozen and the evaporation much retarded; bubbles of gas also often form under the ice, resulting in violent boiling. As a thermometer plunged in the liquid would be inadmissible when the solid residue is required, the temperature may be estimated by means of a pressure gauge (*n*), the temperature corresponding to the pressure being given in the ordinary tables.

After use the sulphuric acid may be boiled in an open flask until it begins to fume. It can thus be used any number of times.

This modification of the apparatus is very efficient for drying solids. Salts very quickly lose their water of crystallisation, and this without fusion even at 100°, and the prevention of access of air may often prove advantageous. Magnesic sulphate thus loses 6 molecules of water at 100°, whereas it requires a temperature of 150° at the ordinary pressure. Sodic carbonate can also be well dried in this manner, although when a large quantity of the salt is placed in the dish, its bad conductivity prevents the access of heat to the interior of the mass. 170 grams of crystallised sodic carbonate lost all but 2 per cent.

of the water in 12 hours; about 6 hours after the commencement of the operation the apparatus was opened, the salt powdered and dried for another 6 hours.

Although the use of this method of evaporation and drying cannot be said to be free from objections, yet possibly its description may prove of some value to those who may be experimenting in this direction.

LV.—*On the Specific Gravity of Paraffin, Solid, Fused, and in Solution.*

By George Beilby.

The paraffin experimented with was obtained from crude shale oil by the process ordinarily used in paraffin oil refineries; it was purified by being four times crystallised from shale naphtha, steamed to get rid of the last traces of naphtha, and filtered through animal charcoal. It was pure white, had a distinctly crystalline fracture, and its fusing point was 38°.

As the solid paraffins dissolve freely, and without the suspicion of chemical action, in the liquid paraffins and olefins with which they occur in crude shale oil, the conditions seemed unusually favourable for a comparison of the specific gravities of the same substance in the three states, solid, fused, and dissolved.

The solvent used was a paraffin oil of sp. gr. 885 at 15·5°. This oil was prepared from crude shale oil by the refining process before referred to, that is, by fractional distillation alternated with treatments by oil of vitriol and caustic soda, the solid paraffins being separated from the liquid by crystallisation and pressing at a low temperature (0°).

The solvent oil was of a pale yellow colour, about three times as viscous as water at 15·5°, and consisted of a mixture of olefins and paraffins boiling between 330° and 400°.

Specific Gravity of the Solid Paraffin.

A mixture of methylated spirit and water was made, such that at 21° a piece of the paraffin at the same temperature would float in it perfectly submerged. The specific gravity of the mixture was taken both by the flask and with a carefully checked hydrometer. The sp. gr. of the mixture, and therefore of the solid paraffin, was 874 at 21°. Numerous trials were made to test the accuracy of this method,

and it was found that it could be depended on to give results accurate to $\frac{1}{1500}$.

Specific Gravity of the Dissolved Paraffin.

The temperature of the room in which the experiment was made was 21° ; the apparatus, paraffin, and solvent oil, having been for some hours in the room, were all at the same temperature. 55·5 grams of paraffin were placed in a 1000 c.c. flask, which was quickly filled up to the mark with solvent oil, care being taken that no air bubbles were allowed to lodge on the paraffin. The flask was slightly warmed and frequently shaken to hasten the solution, which, however, took several hours to complete itself. The solution was now allowed to cool down to 21°, and the volume was noted by a graduated scale on the narrow neck of the flask. The increase of volume was 6·50 c.c.; this, therefore, was the expansion of 55·5 grams on passing from the solid state into solution.

The original volume of 55·5 grams of solid paraffin was 63·26, for—

$$874 : 1000 : : 55{\cdot}5 : 63{\cdot}26.$$

The volume after solution was 63·26 + 6·50 = 69·76 c.c.; therefore the specific gravity of the dissolved paraffin was 795·6, for—

$$69{\cdot}76 : 55{\cdot}5 : : 1000 : 795{\cdot}6.$$

Specific Gravity of the Fused Paraffin.

The specific gravities of the paraffin at its fusing point, 38°, and at a number of points above it, were taken both in the flask and by the hydrometer, all the usual precautions being carefully observed; they were as follows:—

At	38·0°	sp. gr. 783
„	43·4	„ 779
„	49·0	„ 775
„	54·5	„ 771
„	60·0	„ 767
„	65·5	„ 763

The difference in sp. gr. for a rise of temperature of 27·5° is 20. Therefore—

$$\left.\begin{matrix}+\\-\end{matrix}\right\} 1{\cdot}375^\circ \text{ T.} = \left.\begin{matrix}-\\+\end{matrix}\right\} 1^\circ \text{ sp. gr.}$$

From these data we may calculate the sp. gr. of paraffin liquid by fusion at 21°, and so complete the comparison of its sp. grs. in the three states—

The sp. gr. at the fusing point 38° is 783·0.

At 21° it would be $783 + \frac{17}{1{\cdot}375} = 795{\cdot}4$.

Specific Gravity of Paraffin in the Three States.

Solid at 21°	874·0
Dissolved at 21°.....	795·4
Fused (calculated to 21°)	795·6

LVI.—*On Homologous Spectra.*

By W. N. Hartley, F.R.S.E., Professor of Chemistry, Royal College of Science, Dublin.

In June, 1881, I presented to the Chemical Society a "Note on certain Photographs of the Ultra-violet Spectra of Elementary Bodies" (*Chem. Soc. J.*, **41**, 84). Photographs were published with the note, and attention was particularly directed to the extraordinary similarity between the groupings of lines in the spectra of magnesium, zinc, and cadmium, copper, silver, iron, cobalt, and nickel. It was rendered evident that the spectra of elements of the same homologous series present either homologous* spectra or homologous groups of lines in their spectra; but it was remarked, "Whether there are numerical relations between the wave-lengths of different groups of lines, it will be hopeless to determine until the spectra have been reproduced on an enlarged scale, and the wave-lengths for the principal lines of the different elements calculated."

Similarities in the visible spectra of zinc and cadmium, of calcium, strontium, and barium, and in those of the alkali metals were observed by N. Mitscherlich (*Pogg. Ann.*, **121**, 459) and by Lecoq de Boisbaudran (*Spectres Lumineux*). From the observations of the spectra of 31 elements, Ciamician was led to the conclusion that in the spectra of chemically related elements there is a correspondence between single lines or groups of lines. Each natural group of elements has its own peculiar spectrum, and certain lines and groups of lines recur with decrease or increase of wave-length for differences in the spectra of different elements of any one group. Almost every element has a number of feeble lines which bear the same relation to

* Homologous, *i.e.*, possessing an affinity depending on structure or constitution.

the chief line or lines which the over-tones in music bear to the fundamental note.

An increase of wave-length of homologous lines of similar elements corresponds with a greater intensity of chemical kinetic energy (*Intensität der Chemischen lebendigen Kraft*). (*Über die Spectren der Chemischen Elemente und ihrer Verbindungen. Sitzungsberichte der Kaiserlichen Akademie, Wien*, **76**, 499). These observations refer only to the visible rays, or about one octave of the spectrum, but photographs of the ultra-violet region may be easily extended to two octaves above the least refrangible red line, and thus similarities in spectra not hitherto discernible have been made apparent. The conclusions of Ciamician just quoted are completely confirmed by photographs of the ultra-violet region. Dr. G. Johnston Stoney has shown (*Proc. Royal Irish Academy*, **1**, Series II, p. 107) that the spectra of gases are to be referred to faradic motions within the individual molecules, and not to the irregular journeys or encounters of the molecules with each other. The three hydrogen lines, *h*, F, and C, are shown to be the 32nd, the 27th, and the 20th harmonics of a fundamental vibration whose wave-length is 0·013127714 of a millimetre. There is evidently a harmonic relation between the lines in the spectra of magnesium, zinc, cadmium, aluminium, and in calcium, strontium, and barium, when two octaves of the spectra are examined. The fundamental vibrations appear to be in the infra-red region.

It was my original intention to bring forward an extended series of observations on the constitution of the spectra of metallic and non-metallic elements, but from a note in the Journal of this Society, Abstr., **44**, 262, it seems possible that Professors Liveing and Dewar may be engaged in prosecuting a similar line of research, and I beg therefore to be allowed to lay before the Chemical Society such details concerning the published photographs as are now in hand.

Mr. W. E. Adeney has been engaged in collaboration with me in accurate determinations of the wave-lengths of lines in 20 spectra, and a few of our numbers have been employed in the following calculations, but a complete series of measurements of 16 of these spectra have been submitted to the Royal Society. In order that harmonic relations between lines and groups of lines may be conveniently studied, it is necessary to map spectra according to their *inverse wave-lengths* or *oscillation frequencies* instead of in the usual manner. The inverse wave-lengths of the chief rays in the spectra of magnesium, zinc, cadmium, copper, silver, silicon, boron, and aluminium have been mapped. In cases where measurements have not been made independently of the visible rays, I have availed myself of M. Lecoq de Boisbaudran's numbers and calculated the reciprocals therefrom. In every case independent calculations were made, though some of the

numbers might have been taken from the British Association Catalogue of Oscillation Frequencies of Solar Rays (Dublin Report, 1878, p. 40). In this catalogue a small correction, varying with the refrangibility of the rays, is applied to the reciprocals to eliminate the effect caused by the dispersion of air at 760 mm. barometric pressure, and a temperature of 16° C. Generally speaking, the first four figures are not affected by this correction.

The following are the descriptions of the several spectra. The lettering of the groups refers to the mass. Single lines are generally denoted by A and α, and when they recur they are distinguished by affixed numbers. Groups of lines, as pairs or triplets, are denoted by b, or b^1, b^2, and so on. An interval of 10 oscillations corresponds with the space of a millimetre, and the drawing is made with sufficient care as to indicate an interval between two lines equivalent to a difference of only one wave per millimetre, as for instance in the case of the boron, 4004 and 4005.

All lines included between 1500 and 2250 have been the subject of previous investigation, as they are within the range of the visible spectrum; beyond this upper limit lie the ultra-violet rays. Two maps have been published of the spectra of this region, namely, that of Mascart, of the cadmium lines (*Annales de l'École Normale*, 1864), and that of Liveing and Dewar, of the magnesium spectrum (*Proc. Roy. Soc.*, **32**, 189), both on the scale of wave-lengths.

The Magnesium Spectrum.

Table of Oscillation Frequencies.

The series of triplets—

Oscillation frequencies.	
(1.) 1928·9	b^1.
(2.) 1932·9	
(3.) 1934·5	
(1.) 2605·5	b^2.
(2.) 2609·9	
(3.) 2611·9	
(1.) 2997·1	b^3.
(2.) 3001·0	
(3.) 3003·0	
(1.) 3228	b^4.
(2.) 3234	
(3.) 3236	

A pair—

Oscillation frequencies.	
3412·8	c.
3415·0	

Single lines—

1809 a^1
2232 a^2
*3507 a^3

* Concerning this line 3507 a^3 (λ = 2851·3, Hartley and Adeney, or 2852, Liveing and Dewar) the following observation has been made: "The great line of magnesium at wave-length 2852 certainly seems a fundamental one, if we may judge by

Intervals between the oscillation frequencies of the first, second, and third vibrations in the groups b^1 and b^2, b^2 and b^3, b^3 and b^4 respectively:—

	(1.)	(2.)	(3.)
Differences b^1 and b^2....	677·1	677	677·4
,, b^2 and b^3....	391·2	391·1	391·1
,, b^3 and b^4....	230·9	233	233

Interval between individual lines in the four series of triplets:—

b^1.	b^1.	b^2.	b^2.
1934·5 (3)	1932·9 (2)	2611·9 (3)	2609·9 (2)
1932·9 (2)	1928·9 (1)	2609·9 (2)	2605·0 (1)
1·6	4·0	2·0	4·9

b^3.	b^3.	b^4.	b^4.
3003 (3)	3001 (2)	3236 (3)	3234 (2)
3001 (2)	2997 (1)	3234 (2)	3228 (1)
2	4	2	6

The quadruple group—

Oscillation frequencies.

(1.)	3569	d.
(2.)	3575	
(3.)	3578	
(4.)	3584	

The quintuple group—

Oscillation frequencies.

(1.)	3594	e.
(2.)	3596	
(3.)	3598	
(4.)	3601	
(5.)	3602	

its persistence, strength, and facility of reversal." ("On Circumstances producing the Reversal of Spectral Lines," *Proc. Camb. Philos. Soc.*, **4**, Part 5, 265.) This remark seems to apply more particularly to the arc spectrum, for the strongest and most persistent lines observed when a condensed spark is used are those with wave-lengths 2801·6 and 2794·1, the first and third of the quadruple group. If a^3 is a fundamental vibration of the magnesium molecule, it is remarkable that there is an absence in the zinc and cadmium spectra of any line corresponding to it.

The Zinc Spectrum.

Oscillation frequencies.

1571 a single line.

Groups of triplets—

(1.)	2079	b^1.
(2.)	2118	
(3.)	2136	
(1.)	2989	b^2.
(2.)	3028	
(3.)	3046	
(1.)	3571	b^3.
(2.)	3609	
(3.)	3629	

A pair—

	3910	c.
	3997	

Quadruple group—

Oscillation frequencies.

(1.)	4752	d.
(2.)	4757	
(3.)	4764	
(4.)	4771	

Quintuple group—

(1.)	4795	e.
(2.)	4813	
(3.)	4834	
(4.)	4848	
(5.)	4852	

Intervals between the first, second, and third lines in groups b^1, b^2, b^3 of zinc :—

Oscillation frequencies.

(1.)	(2.)	(3.)
2989	3028	3046 b^2
2079	2118	2136 b^1
910	910	910

Oscillation frequencies.

(1.)	(2.)	(3.)
3571	3609	3629 b^3
2989	3028	3046 b^2
582	581	583

Intervals between the individual lines in the groups b^1, b^2, b^3 of zinc :—

b^1.	b^1.	b^2.	b^2.	b^3.	b^3.
(3.) 2136	(2.) 2118	(3.) 3046	(2.) 3028	(3.) 3629	3609
(2.) 2118	(1.) 2079	(2.) 3028	(1.) 2989	(2.) 3609	3571
18	39	18	39	20	38

It is worthy of remark that the difference between the groups b^1 and b^2 + that between b^3 and b^4 in the magnesium spectrum, yield the number 910, the difference between groups b^1 and b^2 of zinc. Only by taking great care can the extreme groups of rays d and e in the

spectrum of zinc be photographed. Films particularly sensitive to the rays in this region may be prepared, upon which they may be photographed without difficulty.

The Cadmium Spectrum.

In the cadmium spectrum two lines, numbered by M. Mascart 9 and 10, are in reality double lines, with some measurable distance in wave-length. Then taking the wave-lengths of the two lines constituting No. 9 as 3612·5 and 3610, we have for the number of oscillations occasioned by each ray 2765 and 2770. The wave-length adopted for No. 10 are 3467·4 and 3465·7, giving for the oscillation frequencies 2884 and 2882.

A single line—

Oscillation frequencies.

1553 *a*.

A pair—

3639 } *c*.
3809 }

Triplets—

(1.) 1966 }
(2.) 2083 } b^1.
(3.) 2138 }

(1.) 2765—2770 }
(2.) 2884—2882 } b^2.
(3.) 2938 }

(1.) 3355 }
(2.) 3472 } b^3.
(3.) 3525 }

Quadruple group—

Oscillation frequencies.

(1.) 4292 }
(2.) 4307 } *d*.
(3.) 4322 }
(4.) 4334 }

Quintuple group—

(1.) 4369 }
(2.) 4413 }
(3.) 4461 } *e*.
(4.) 4535 }
(5.) 4555 }

Intervals between the first, second, and third lines in the groups b^1, b^2, and b^3 of cadmium :—

(1.)	(2.)	(3.)
2767·5	2883	2938 b^3
1966·0	2083	2138 b^1
801·5	800	800
3355	3472	3525 b^3
2767	2883	2938 b^2
588	589	587

Intervals between the individual lines in the three groups of triplets in the spectrum of cadmium :—

b^1.		b^1.		b^2.		b^2.		b^3.		b^3.	
(3.)	2138	(2.)	2083	(3.)	2938	(2.)	2883	(3.)	3525	(2.)	3472
(2.)	2083	(1.)	1966	(2.)	2883	(1.)	2767·5	(2.)	3472	(1.)	3355
	55		117		55		115·5		53		117

THE SPECTRUM OF COPPER.

Oscillation frequencies.

1906, 1959	α^1. Pair.
3054, 3079	α^2. Pair.
3675, 3678, 3685, 3700, 3703, 3719	β-Group.
3929, 3954, 3958, 3990, 4013, 4017, 4020	γ-Group.

THE SPECTRUM OF SILVER.

Oscillation frequencies.

1830, 1919	α^1. Pair.
2985, 3051	α^2. Pair.
3404, 3408, 3414, 3446, 3453, 3481	β-Group.
3688, 3759, 3765, 3805, 4032, 4037, 4043	γ-Group.

THE SPECTRUM OF ALUMINIUM.

A spectrum of the second order, taken from solutions and from metallic electrodes:—

Oscillation frequencies.

(1.) 1601, (2.) 1603 — Pair b^1.

Difference (1.) 924. (2.) 927. — 1788 a^1. Isolated ray.

(1.) 2525, (2.) 2530 — Pair b^2. Difference 1002.

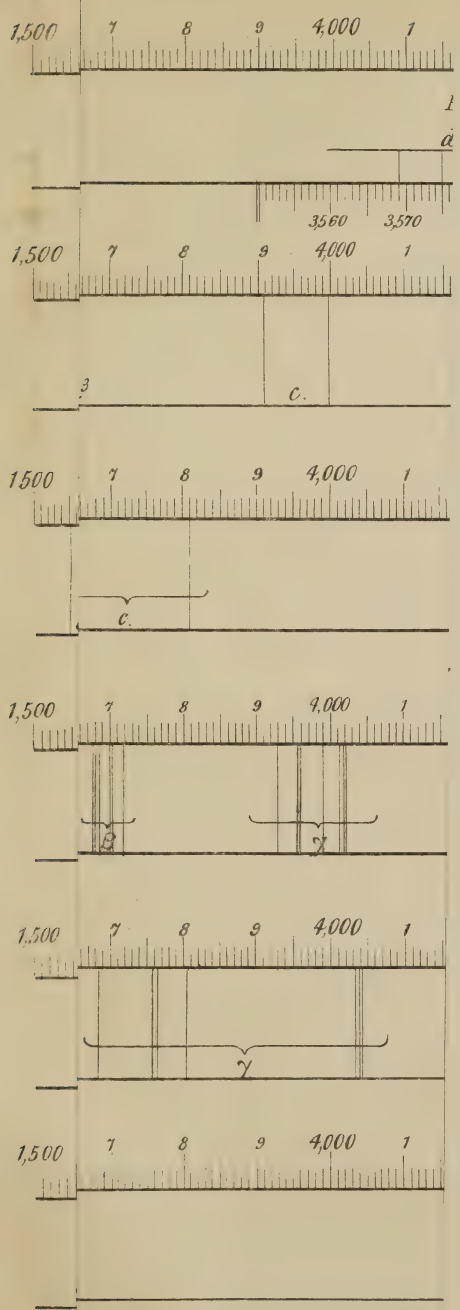
Difference (1.) 708. (2.) 747. — 2790 a^2. Isolated ray.

(1.) 3233, (2.) 3277 — Pair b^3. Difference 762.

3552 a^3. Isolated ray.

The pair b^2 are the aluminium lines lying between 1 + and K on M. Cornu's map of the solar spectrum. There are some lines of greater refrangibility than those given above, which, however, are readily

REQUENCIES.


1,500
7
8
9
4,000
1
a
3560
3,570
1,500
7
8
9
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c.
1500
7
8
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4,000
1
c.
1,500
7
8
9
4,000
1
3
γ
1,500
7
8
9
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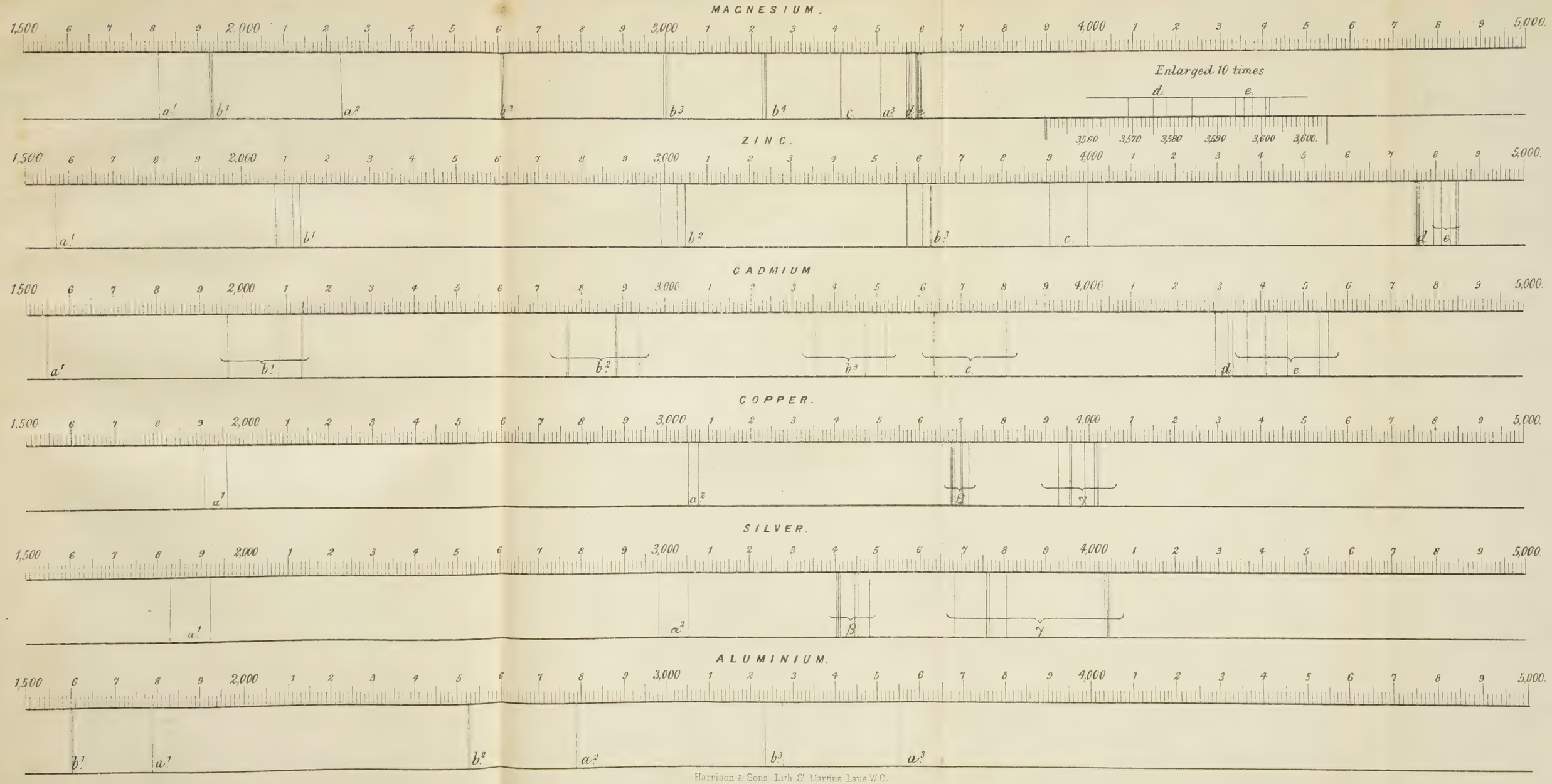
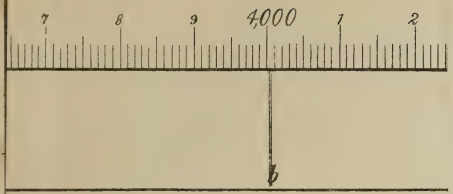
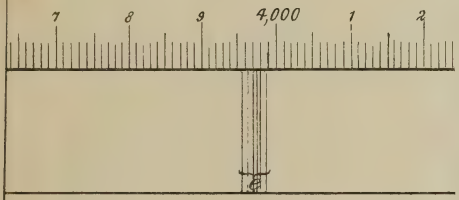
γ
1,500
7
8
9
4,000
1

SPECTRA MAPPED ACCORDING TO OSCILLATION FREQUENCIES.



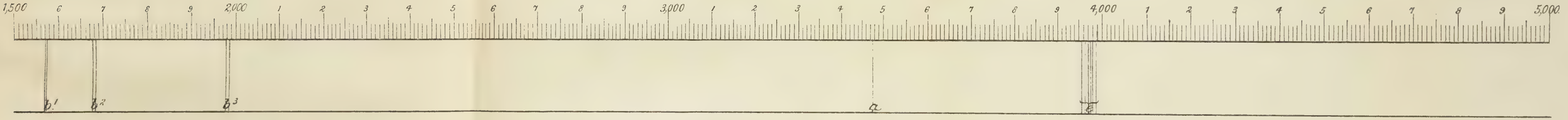
Harrison & Sons, Lith. St Martins Lane W.C.


7
8
9
4,000
1
2
b


7
8
9
4,000
1
2
a

BORON.

SILICON.



Lith. St Martin

absorbed by air (Cornu, *Archives des Sciences Physiques et Naturelles* [3], **2**, 112—126).

The intervals between the lines of the quintuple groups of magnesium, zinc, cadmium, and silicon are the following:—

Mg.	Zn.	Cd.	Si.
2	18	44	8
2	21	48	8
3	14	74	7
1	4	20	12

A relationship is observable between the Mg and Cd, but not between the other elements; doubtless more accurate determinations of these measurements are required.

The Spectrum of Boron.

To ascertain the relation of the spectrum of the 2nd Order of boron to those of beryllium and magnesium, borax in strong solution was submitted to the action of a condensed spark, and photographs of its spectrum were observed. The lines are strong and well marked, and apparently all of equal intensity. The least refrangible ray in the map is taken from Schützenberger's *Traité de Chimie Générale*, **1**, 508.

Oscillation frequencies.

1721 a^1. An isolated ray.
2898 a^2. An isolated ray.
4004, 4005 } b. A pair.

The Spectrum of Silicon.

The spectrum of silicon of the 2nd Order was obtained by taking sparks from a strong solution of sodium silicate, and photographing the rays. In addition to the lines mapped out, others of unequal intensity have been identified with silicon. The object in observing silicon was to verify if possible the statement of Ciamician concerning the compound nature of its spectrum and the relation of boron, beryllium, and carbon, to aluminium, magnesium, silicon, and oxygen. In addition to this spectrum three pairs of visible lines have been observed (Schützenberger, *Traité de Chimie Générale*, **1**, 536), and these also are inserted in the map.

Pairs— Oscillation frequencies.		
1570, 1574	b.	
1668, 1675	b^2.	
1977, 1984	b^3.	

Oscillation frequencies.		
3471	a^1.	An isolated ray.
3800	a^2.	An isolated ray.
3935, 3955, 3962, 3970, 3975, 3978, 3990	e.	A fine group.
4105	a^3.	An isolated ray.

The foregoing data present a considerable addition to the body of evidence in support of the view that elements whose atomic weights differ by a constant quantity, and whose chemical character is similar, are truly homologous, or in other words, are the same kind of matter in different states of condensation. It will be remembered that Mr. Norman Lockyer (*Proc. Roy. Soc.*, **28**, 157) has proposed to explain the occurrence of several coincident lines in the spectra of different elements by supposing that each spectrum is composed of several spectra, and that these compound spectra are the spectra of compound bodies, and not of elements. The action of a low temperature causes the vibration of a compound molecule, while the action of a high temperature causes a breaking up of the molecule either into smaller molecules of the same element, or into those of distinct elements. It appears also from the way in which he has treated the subject, that every elementary substance may be decomposed into as many simple substances as there are rays in its spectrum. I allude here to the observations concerning the lines in the spectra of iron, calcium, magnesium, lithium, and hydrogen. M. Lecoq de Boisbaudran (*Compt. rend.*, **73**, 943; and **82**, 1264), also Vogel (*Ber.*, **13**, 274), and Van Monckhoven (*Compt. rend.*, **95**, 520), have disposed of some of these facts upon which this theory is founded. With even very moderate dispersive power, something like 1200 lines can be recognised in the spectrum of iron, an element which has an atomic weight of 56, and it is simply inconceivable that a body of the chemical nature of iron can have a molecular structure so complex as to be composed of 1200 different simpler substances. Mr. Lockyer's hypothesis seems quite incompatible with the theory that the spectra are composed of harmonic vibrations, because a compound body would give two or more series of harmonics related to two or more fundamental vibrations, and elements having a common component should give spectra in which the same series or groups of lines should appear. If therefore we are to draw inferences as to the compound nature of substances from coincident lines in their spectra, it is not single lines but harmonic

series that we must look to for coincidences. I will give an illustration of this reasoning as applied to the spectra of tellurium and copper, in which appear the following lines:—

Copper. Wave-lengths.	Tellurium. Wave-lengths.
3307·4	3307·5
3290·2	3290·0
3280·5	3280·4 (very strong)
3273·6 (very strong)	3273·8 (very strong)
3264·3	3264·4
3247·3 (very strong)	3247·2 (very strong)

It is impossible to say whether these lines are coincident or not, as we cannot feel certain of the correctness of our measurements to 0·1-tenth meter, though they are believed to be correct to 0·2. It appeared at first sight that the copper contained tellurium, which it was impossible to separate; but this was soon seen not to be the case, because of two of the longest and strongest lines, 3280·4 and 3382·7, in the tellurium spectrum; the former was represented by a comparatively very weak line, and the latter was not represented at all. If copper, on the other hand, were contained in tellurium, either as a constituent of the element or as an impurity, the pair of lines α^2 should be followed by the groups β and γ, or preceded by α^1. It is upon the recurrence of such groups of lines in spectra that Ciamician has based his conclusion that silica is composed of carbon and oxygen, with a corresponding atomic weight, 12 + 16 = 28, and aluminium of boron and oxygen, 11 + 16 = 27 (*Berichte der Kaiserlichen Akademie, Wien*, **72**, 138–44, 1880). It is to be regretted that Dr. Ciamician's maps of spectra refer to an arbitrary scale and not to wave-lengths, as several of the groups of lines which he has drawn appear to recur in the ultra-violet region; for example, the group which he designated by *b* in tellurium, and several in arsenic and antimony. It is doubtful whether the group of lines belonging to silicon which I have mapped is homologous with a somewhat similar group belonging to Ciamician's spectrum of silicon.

The probability of many of the fundamental vibrations of the simpler elements being found in the infra-red region will no doubt soon be put to the test of experiment, since we have Captain Abney's method of photography applied to these rays, and Professor Rowland's method of spectrum analysis by means of concave ruled specula, unequalled for dispersion and exquisite definition, giving us a range of at least four octaves. Professor Langley has shown that there are two octaves of vibrations below A (*Archives des Sciences Physiques et Naturelles*, 9,

95, January, 1883), and M. Cornu has photographed lines of aluminium one octave above wave-length 3700. I hope in a future communication to return to this subject.

LVII.—*Thioxalic Ether.*

By H. Forster Morley, D.Sc., and W. Johnston Saint.

Five years ago one of us endeavoured, in the laboratory of Professor Kekulé, to prepare an acid ethereal salt of the unknown thioxalic acid by acting on chloroxalic ether with sulphuretted hydrogen—

$$ClCO.CO.OEt + H_2S = HCl + HS.CO.CO.OEt.$$

The attempt was, however, unsuccessful.

Nevertheless we thought that, considering the interest which attaches to the derivatives of thiacetic and the various thiocarbonic acids, it was worth while to prepare corresponding derivatives of oxalic acid.

Chloroxalic ether acts readily on mercaptan in the following manner:—

$$ClCO.CO.OEt + HSEt = HCl + EtS.CO.CO.OEt.$$

It is best to add the mercaptan in small quantities, and to cool the flask containing the mixture in ice-cold water, the heat developed by the reaction being very considerable. When the calculated quantity of mercaptan has been added, the product is heated to boiling (an inverted condenser being attached to the flask), when torrents of hydrochloric acid are disengaged; the liquid is then distilled. The first portion, which comes over at 128° C., is unaltered chloroxalic ether; the thermometer then rises quickly to 210°, the rest coming over between 210° and 212°. This high-boiling liquid still contains mercaptan and chloroxalic ether, from which it is freed by repeated distillation. The purified substance boils at 211° (uncorr).

The combustion was effected with a mixture of coarsely powdered lead chromate and copper oxide.

I. 0·1575 gram substance gave 0·2565 gram CO_2 and 0·0890 gram H_2O.

II. 0·221 gram substance gave 0·3585 gram CO_2 and 0·126 gram H_2O.

It was not found possible to determine the sulphur by Carius's method, which gave only about 0·1 per cent.; accordingly we resorted to a modification of the method recently described by Plimpton and Graves for the estimation of chlorine (this Journal, **41**, 119). We employed potash free from sulphate to absorb the products of combustion, and found that 0·226 gram of substance produced 0·3328 gram baric sulphate. The combustion lasted half an hour, and we found by a subsequent experiment that our coal-gas produced 0·0162 gram $BaSO_4$ when burning under the same conditions for a like interval. Deducting this, we find 0·3166 gram as the amount of sulphate formed by the combustion of the above quantity of substance.

From these data the following results are calculated:—

	Found.			Calculated for $C_6H_{10}SO_3$.
	I.	II.	III.	
C.....	44·41	44·24	—	44·44
H.....	6·28	6·33	—	6·17
S.....	—	—	19·24	19·75

Thioxalic ether is a colourless liquid, having a faint odour like that of garlic, a specific gravity of 1·1446 at 0°: it boils at 217° C. (corr.). Aqueous potash readily decomposes it, especially on warming, in accordance with the equation—

$$EtS.CO.CO.OEt + 2KHO = K_2C_2O_4 + EtSH + EtOH.$$

The quantity of oxalic acid produced in this way was determined by adding calcium chloride to the solution acidified with acetic acid, and igniting the precipitate.

I. 0·5344 gram substance gave 0·3270 gram $CaCO_3$.
II. 0·5195 „ „ 0·3181 „ „

The amount of hydric oxalate produced by the decomposition of thioxalic ether is found therefore to be—

	I.	II.	Calculated.
$H_2C_2O_4$.....	55·01	55·11	55·56

Thioxalic ether sinks in water and decomposes slowly into oxalic acid, alcohol, and mercaptan; the decomposition is more rapid if the temperature be raised. On exposure to moist air, it changes to a crystalline mass of oxalic acid.

On passing dry ammonia into thioxalic ether an odour of mercaptan is developed, whilst the liquid quickly solidifies. The solid mass when crystallised from spirit has the characteristic appearance of oxamethane, and melts at 112°. Oxamethane melts at 110°.

Ammonia therefore decomposes thioxalic ether into mercaptan and oxamethane—

$$EtS.CO.CO.OEt + NH_3 = HSEt + NH_2.CO.CO.OEt.$$

While we have little hope of obtaining thioxalic acid itself, we thought it probable that thioethyloxalic acid might be formed by the action of alcoholic potash on thioxalic ether—

$$EtS.CO.CO.OEt + KOH = EtOH + KS.CO.CO.OEt.$$

We added the calculated quantity of caustic potash dissolved in absolute alcohol to an alcoholic solution of thioxalic ether; the liquid was at once filled with pearly crystalline plates, but mercaptan was also produced.

The crystals were separated from the liquor, recrystallised from dilute alcohol, and ignited.

I. 0·1500 gram substance gave 0·0662 gram potassic carbonate.
II. This treated with sulphuric acid gave 0·0825 gram potassic sulphate.

From these data the percentage of potassium is found to be—

	I.	II.	Calculated for $K(C_2H_5)C_2O_4$.
K.....	24·93	24·67	25·00

The crystals are therefore potassic ethyl oxalate, and in fact qualitative analysis shows them to be free from sulphur. The decomposition, therefore, takes place thus:—

$$EtS.CO.CO.OEt + KOH = EtSH + KO.CO.CO.OEt.$$

Although thioethyloxalic acid cannot be prepared in this way, it is of course possible that by employing an alcoholic solution of potassic sulphydrate instead of potash it may yet be obtained.

An attempt to prepare thioxalic ether by distilling oxalic ether over pentasulphide of phosphorus was not successful, the ether not being attacked. We do not, however, regard this experiment as conclusive, as we were subsequently astonished to find that neither commercial pentasulphide (from Kahlbaum) nor a specimen which we ourselves prepared by heating amorphous phosphorus and roll-sulphur together, had any action on acetic ether, although it is well known that Kekulé long since showed that these substances act with violence on one another, producing thiacetic ether.

These experiments were made in the laboratory of University College, London.

LVIII.—*On the Condensation-products formed by Benzoic Aldehyde with Malonic and Isosuccinic Acids.*

By Charles M. Stuart, B.A.

When Perkin first published his researches upon the condensation occurring between aromatic aldehydes and bodies of the acetic series of acids, he used a mixture of an anhydride with the sodium salt of the same acid, and considered that the condensation took place between the aldehyde and the anhydride, the sodium salt playing only a secondary part.

Fittig used acetic anhydride both with sodium succinate and with sodium pyrotartrate (*Ber.*, **14**, 1825), and as he obtained condensation-products derived from succinic and pyrotartaric acids, he considered that the condensation took place between the aldehyde and the sodium salt, the anhydride acting only as a water-withdrawing agent. At the same time he expressed his opinion that a condensation similar to that of aldol took place, resulting in the formation of a hydroxy-acid, which, by separation of water, produced an unsaturated acid. For example, benzoic aldehyde and sodium acetate produced, according to this view, phenyl-β-lactic acid, which, by separation of water, gave cinnamic acid.

Later, in conjunction with Jayne (*Annalen*, **216**, 118), he produced hydroxypivalic acid by the use of sodium succinate. It was, however, objected by Tiemann (*Ber.*, **16**, 2061) that in these experiments decomposition took place between the sodium salt and acetic anhydride, resulting in the formation of sodium acetate and the anhydride of the acid corresponding with the sodium salt, and that the latter then combined with the aldehyde. This objection was foreseen by Fittig (*Annalen*, **216**, 115), who promised an account of a series of experiments showing that condensation took place between benzoic aldehyde and such acids as malonic and isosuccinic employed in the form of sodium salts, under which circumstances the formation of an anhydride was out of the question.

Claisen had already found that condensation took place between malonic ether and benzoic aldehyde when they were treated with a stream of hydrochloric acid gas (*Ber.*, **14**, 348). It seemed to us desirable, by the use of sodium malonate, to imitate more precisely the conditions of Perkin's original work. While the investigation was proceeding, a separate paper, "Sur la Reaction de Perkin," read by Crismer before the Belgian Academy, and containing a complete account of Claisen's work, was put into our hands. This paper con-

tained an account of the benzalmalonic acid described by us below. When our work was nearly ready for publication, Claisen's paper appeared in the *Annalen* (**218**, 129), in which, in conjunction with Crismer, he gave further particulars of his work. This led to Professor Fittig publishing the short notice which appeared in the *Berlin Berichte* (**16**, 1436).

Sodium malonate, acetic anhydride, and benzoic aldehyde were mixed together, in proportions corresponding with equal molecules of the substances. To our astonishment the mixture began to harden and give off carbon dioxide at ordinary temperatures, and in a few days the whole had become a solid mass. It was then mixed with water, and exhausted with ether, the aqueous solution contained only sodium malonate. The ethereal solution was neutralised with sodium carbonate, and the benzoic aldehyde separated by means of ether; the sodium carbonate solution then gave a copious precipitate of cinnamic acid on addition of hydrochloric acid. The experiment repeated several times always gave the same result. Here the formation of cinnamic acid might be due to the condensation of the aldehyde, either with the malonate or with the acetic anhydride. In order to decide upon this point, sodium isosuccinate was substituted for the malonate. The mixture of isosuccinate, acetic anhydride, and benzoic aldehyde began to harden and give off carbon dioxide exactly as had occurred in the previous experiment. The mass was treated with water and exhausted with ether, and the ethereal solution was shaken with sodium carbonate to separate the benzoic aldehyde, after the removal of which the solution was precipitated with hydrochloric acid; not a trace of cinnamic acid was obtained. The precipitated acid crystallised in needles melting at 78°, and when boiled in water with barium carbonate, gave a barium salt which crystallised in small white needles, and on being analysed gave the following numbers:—

0·4321 gram substance gave 0·586 gram water and 0·1885 $BaSO_4$.

	Calculated for barium phenylcrotonate + $4H_2O$.	Found.
Water	13·55	13·56
Ba	25·80	25·65

This is therefore isophenylcrotonic acid, the same as that obtained by Perkin from benzoic aldehyde and sodium propionate, and by Conrad from the benzyl ether of propionic acid (*Annalen*, **204**, 191); it is formed according to the equation—

$$C_6H_5.COH + CH_3.CH(CO_2H)_2 = C_6H_5.CH:C(CH_3).CO_2H + CO_2 + H_2O,$$

which proves that in Perkin's reaction the condensation takes place, not with the anhydride, but with the sodium salt.

In both these experiments carbonic acid was given off, and a monobasic acid obtained; it seemed therefore desirable to try to moderate the reaction by the use of some substance which should act in the same way as acetic anhydride, but with less violence, and for this purpose glacial acetic acid was chosen. When a mixture of glacial acetic acid with sodium malonate and benzoic aldehyde was heated to 100°, carbon dioxide was given off, and the mixture, treated in the same way as in the previous experiments, produced nothing but cinnamic acid, this time in considerable quantity.

Afterwards it was found that a mixture of these three bodies became solid at the ordinary temperature, and when treated as above, yielded no cinnamic acid. Ether extracted from the solution of the mass in water, nothing but the excess of benzoic aldehyde and acetic acid. The aqueous solution left after extraction was therefore examined; it was acidified with hydrochloric acid and exhausted with ether, and the ethereal solution was distilled from a water-bath kept at 60°. The residue was washed with water to free it from malonic acid, until a specimen placed in water and neutralised with ammonia gave no further precipitate with barium chloride. It was then dried at a low temperature, and crystallised by dissolving it in ether and adding carbon bisulphide. Of a specimen submitted to analysis—

0·2569 gram gave 0·0956 gram H_2O and 0·5859 gram CO_2, which corresponds with

		Theory for $C_{10}H_8O_4$.
C	62·20	62·50
H	4·13	4·16

This is therefore benzalmalonic acid produced in the form of sodium salt, thus:—

$$C_6H_5.COH + CH_2(CO_2Na)_2 = C_6H_5.CH:(CO_2Na)_2 + H_2O.$$

The ether of this acid is described by Claisen, and the acid by Crismer; it melts with evolution of carbon dioxide at 193°, and has the properties ascribed to it by Crismer, only it does not, as he states, precipitate a solution of barium chloride in the cold after being neutralised with ammonia. If, however, the clear solution thus obtained be warmed by placing the vessel containing it in boiling water, a copious formation of small needle-like crystals takes place: this reaction is very characteristic of benzalmalonic acid. The crystals thus obtained were collected and examined.

0·4192 gram substance dried at 130° gave 0·299 gram barium sulphate, which corresponds with

41·93 p.c. barium. Calculated 41·89

They are therefore the barium salt of benzalmalonic acid.

When benzalmalonic acid is boiled with water, it splits up readily into benzoic aldehyde, recognisable by its odour, and an acid having the properties of malonic acid, the calcium salt of which was prepared and examined—

0·3772 gram gave 0·0689 gram water and 0·2885 gram $CaSO_4$.

		Theory for calcium malonate.
Water.....	18·26	18·16
Ca	22·50	23·05

The benzalmalonic acid used by Crismer had been crystallised from water, under which circumstances it is probable that the above decomposition had partly taken place, and that the malonic acid so formed would give a precipitate with barium chloride. The best way of crystallising the acid is to dissolve it in ether, and add an equal volume of carbon bisulphide. As the benzalmalonic acid was always accompanied by a more soluble acid, an experiment was made in which all the operations were conducted at the ordinary temperature, the benzalmalonic acid being separated from the more soluble acid, the silver salt of which was prepared and analysed.

0·5948 gram substance gave 0·4021 gram = Ag 67·60 p. c.
Theory for silver malonate 67·92.

The acid was therefore malonic acid, and no trace of any hydroxy-acid was found.

On attempting to proceed in the same way with sodium isosuccinate, it was found that no action whatever took place when this salt was mixed with benzoic aldehyde and glacial acetic acid at the ordinary temperature. When the mixture was heated to 100° the isosuccinate was entirely decomposed by the acetic acid, carbon dioxide being given off, and propionic acid formed: it seemed therefore desirable to observe what reaction would take place if sodium propionate were at once used with acetic acid.

A mixture consisting of sodium propionate, benzoic aldehyde, and glacial acetic acid, in the proportion of 3 mols. of the latter to 1 of each of the former, was heated, a few drops of acetic anhydride being added to ensure the absence of water. No action took place up to the boiling point of the acetic acid, but on heating to 200° in a sealed tube, pouring the contents into water, and distilling off the excess of benzoic aldehyde with steam, a white precipitate was obtained on cooling, which was increased by the addition of hydrochloric acid. This was filtered off, converted into the barium salt by boiling with

barium carbonate, and repeatedly crystallised. The first crystals on being analysed gave the following numbers :—

0·2098 gram substance gave 0·0285 gram water, and 0·0908 $BaSO_4$.
0·5498 „ „ „ 0·0733 „ „ „ 0·2409 $BaSO_4$.

	I.	II.	Calculated for Barium Isophenylcrotonate + $4H_2O$.
H_2O.....	13·58	13·35	13·55
Ba	25·73	25·76	25·80

The acid recovered from this salt melted at 78°, crystallised in needles, and showed the properties of isophenylcrotonic acid. The formation of this barium salt has not been observed before; it crystallises in small white crystals when the solution is allowed to cool slowly. When the solution was allowed to cool quickly, the other salts described by Perkin and Conrad, and crystallising in transparent plates with 1 mol. of water, were obtained.

The second crop of crystals were analysed, with the following results :—

0·1420 gram substance gave 0·0115 water and 0·0705 $BaSO_4$.

		Theory for Barium Cinnamate.
H_2O	8·09	7·70
Ba	29·19	29·37

The acid recovered from this salt melted at 132°, and showed all the properties of cinnamic acid. The yield of isophenylcrotonic acid was always greater than that of the cinnamic acid.

These experiments show conclusively that in Perkin's reaction the condensation of the aldehyde takes place, not with the anhydride, but with the sodium salt; the anhydride may in fact be completely omitted, and, if present, it complicates the result by the production of secondary reactions. With sodium malonate and isosuccinate, the bibasic acids were always completely decomposed if acetic anhydride was present; and even if a mixture of sodium malonate, acetic anhydride, and acetic acid be shaken together at the ordinary temperature, it gives off carbonic acid, becomes hot, turns yellow, brown, and finally black. We hope to further investigate this remarkable reaction.

It is possible that a hydroxy-acid is first formed in these reactions, but as we have seen that benzalmalonic acid is readily split up on boiling with water, such a hydroxy-acid is probably extremely unstable; we therefore thought that if, instead of benzoic aldehyde we employed its orthonitro-derivative, we might obtain the hydroxy-acid, particularly as Baeyer had shown that the condensation-product of ortho-

nitrobenzoic aldehyde with acetone is a hydroxy-derivative (*Ber.*, **15**, 2856), while that of benzoic aldehyde and acetone is an unsaturated body (*Ber.*, **14**, 2460). Sodium malonate also seemed peculiarly adapted for this purpose, as it unites with aldehyde at ordinary temperatures. To obtain this body it was necessary to prepare ortho-nitrocinnamic acid; this was prepared by Müller (*Annalen*, **212**, 124) by nitrating cinnamic acid, but we found that a better yield of the ortho-compound was obtained by the following process.

Ethyl cinnamate was dropped from a tap-funnel into fuming nitric acid cooled with ice; the temperature must be kept low, sulphuric acid must be avoided, and the solution must not be allowed to stand, but must be immediately poured into ice-cold water. I have found it best to nitrate not more than 10 grams of the ether at once, and then to pour the nitric acid containing this quantity into water. The precipitate in the water must be quite solid, not in the least oily, is filtered off, drained, and washed with cold alcohol, which dissolves the orthonitrocinnamic ether, leaving pure paranitrocinnamic ether. The alcohol of the filtrate is distilled off, and the residue poured into water, when an oil separates, which after few minutes solidifies to a mass of crystals of orthonitrocinnamic ether, which may be pressed between filter-paper, and then at once used for conversion into ortho-nitrobenzoic aldehyde; for this we used the method of Friedlander and Henriques (*Ber.*, **14**, 2803).

In this way from 50 grams of ethyl cinnamate we obtained 22 grams para- and 21 grams ortho-nitrocinnamic ether. The statement in *Watts's Dictionary*, that ethyl cinnamate is scarcely attacked by fuming nitric acid, must therefore be considered as an error. The paranitro-cinnamic ether was also converted into paranitrobenzoic aldehyde. As Claisen found that a good yield of benzalmalonic acid is produced by heating benzoic aldehyde, acetic acid, and malonic acid together to 100°, we used the paranitrobenzoic aldehyde in the same way.

Paranitrobenzoic aldehyde is heated to 60° with malonic acid and glacial acetic acid; after a few hours water is added, and the solution filtered; the precipitate is washed with chloroform, to separate any excess of aldehyde, and crystallised by dissolving it in ether, and adding carbon bisulphide. It melts at 227°, giving off CO_2, and leaving crystals in the capillary tube, which melt again at 286° (m. p. of paranitrocinnamic acid, 288°) (Drewson, *Annalen*, **212**, 151).

Of a specimen burnt and submitted to analysis—

0·387 gram gave 0·1128 water, and 0·7221 CO_2.

	Found.	Calculated for $C_6H_4<^{NO_2}_{CH}=C<^{CO_2H}_{CO_2H}$
C	50·89	50·65
H	3·23	2·95

It is therefore paranitrobenzalmalonic acid. Its solution neutralised with ammonia gives a yellowish precipitate with barium chloride; it can be crystallised from water, but is always partly decomposed into malonic acid and paranitrobenzoic aldehyde, the latter crystallising out with the paranitrobenzalmalonic acid. Some paranitrocinnamic acid was also formed when the solution was evaporated to dryness; this corresponds with the decomposition of benzalmalonic acid with water, in which Claisen noticed the formation of cinnamic acid. As this body was of no theoretical interest, we did not proceed further with its investigation.

With orthonitrobenzoic aldehyde, on the other hand, whether we allowed it to stand with sodium malonate and acetic acid at ordinary temperatures, or warmed it to 60° with malonic acid and acetic acid, we obtained a crystallisable acid soluble in water, which melts at 161° with complete decomposition, being in fact partly carbonised, and, unlike the benzalmalonic acid and its paranitro-derivative, can be boiled with water or dilute acids without the least decomposition. It is not the unsaturated acid, and we are at present engaged in its investigation.

This research was carried out in the laboratory of the University of Strassburg, under the direction of Professor Fittig, to whom I express my most sincere thanks for the kind assistance which he has given me.

LIX.—*A Contribution to the History of the Constitution of Bleaching Powder.*

By L. Trant O'Shea, Assistant Lecturer and Demonstrator in Chemistry in Firth College, Sheffield.

The subject of this paper has attracted much attention from chemists, but it still remains an open question whether the constitution of bleaching powder is represented by Gay-Lussac's original formula $Ca(OCl)_2 + CaCl_2$, or by Odling's modified form of the same, $Ca\begin{cases} OCl \\ Cl \end{cases}$, or by that proposed still more recently by Stahlschmidt, $Ca\begin{cases} OH \\ OCl \end{cases}$ (*Ber.*, 1875, 869; *Dingl. polyt. J.*, **221**, 243, 335).*

At the outset it seems necessary to make some distinction between bleaching powder and the compound at the expense of which oxidation takes place; since, if we accept Gay-Lussac's or Stahlschmidt's formula, bleaching powder consists of calcium chloride mixed respectively with calcium hypochlorite, and $Ca\begin{cases} OH \\ OCl \end{cases}$, which are the oxidising compounds in each case. It is therefore proposed to use the terms "*bleaching compound*," as applied to this oxidising compound, and *bleaching powder* when speaking of the substance obtained by the action of chlorine on calcium hydrate.

That the molecule of the bleaching compound contains the radicle of hypochlorous acid has been placed beyond doubt by the results of Kopfer described in his paper "On the Action of Acids on Bleaching Powder" (this Journal, 1875, p. 713). The subject of doubt lies in the question, Do the elements of water or of calcium chloride enter in any way into the molecule?

In bleaching powder prepared from dry calcium hydrate, there is always present some unconverted calcium hydrate, and although Fresenius, Kolb, and others have proposed complicated formulæ in which account has been taken of its presence, yet these being only empirical, call for no special comment. Stahlschmidt's formula calls for more attention; it is distinctly constitutional, representing the *bleaching compound* as $Ca\begin{cases} OH \\ OCl \end{cases}$, in which the elements of water take part, whilst he represents the formation of *bleaching powder* thus:

$$3Ca\begin{cases} OH \\ OH \end{cases} + 2\begin{cases} Cl \\ Cl \end{cases} = 2Ca\begin{cases} OH \\ OCl \end{cases} + CaCl_2 + 2H_2O.$$

* See, however, *Liebig's Annalen*, **219**, 129.

According to such a view, bleaching powder contains free calcium chloride; and the strongest bleaching powder that it is possible to prepare must and can have only the composition—

$$2(\mathrm{Ca}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OCl}\end{matrix}\right) + \mathrm{CaCl_2}.$$

Odling's modification of Gay-Lussac's formula presupposes the non-existence of free calcium chloride in bleaching powder, and this is stated by Schorlemmer (*Ber.*, **7**, 682) to be confirmed by the fact that when the powder is washed with successive small quantities of water, the first washings contain only a slight excess of chlorine, whereas the subsequent ones contain calcium and chlorine in the proportion 1 : 2. But on the other hand this formula takes no account of the excess of calcium hydrate always present in bleaching powder.

If either of the above formulæ be taken, they can be resolved thus:—

$$2\mathrm{Ca}\left\{\begin{matrix}\mathrm{OCl}\\ \mathrm{Cl}\end{matrix}\right. + x\mathrm{Ca(OH)_2} = \mathrm{Ca(ClO)_2} + \mathrm{CaCl_2} + x\mathrm{Ca(OH)_2}.$$

$$2\mathrm{Ca}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{Cl}\end{matrix}\right. + \mathrm{CaCl_2} = \mathrm{Ca(OCl)_2} + \mathrm{CaCl_2} + 2\mathrm{Ca(OH)_2}.$$

Or if we presuppose the correctness of Odling's formula, Stahlschmidt's may be written $2(\mathrm{Ca}\left\{\begin{matrix}\mathrm{OCl}\\ \mathrm{Cl}\end{matrix}\right) + \mathrm{Ca(OH)_2}$.

In the first place, therefore, it is necessary to establish the proportion between the numbers of molecules of calcium hypochlorite, calcium chloride, and calcium hydrate in dry bleaching powder; in the second to determine the existence of free calcium chloride; and in the third to ascertain the composition of the residue after removal of the calcium chloride if any be present.

In carrying out this research the several samples of bleaching powder were prepared as follows from pure lime:—

Pure lime freshly ignited and free from calcium carbonate, was hydrated by mixing it in a flask with the requisite quantity of water, and well shaking. When the water was absorbed, the powder was well pounded, placed in a stoppered bottle, left at rest for 18 to 24 hours, again well pounded and mixed, and the hydrate in it determined.

Three different samples were prepared—

A, containing	23·7	per cent.	H_2O.
B	,, 21·27	,,	,,
C	,, 39·02	,,	,,
$Ca(HO)_2$ requires	24·31	,,	,,

To prepare the bleaching powder, a weighed quantity of hydrate was thinly spread on a shallow dish and placed in a bell-jar, which was connected with a chlorine apparatus, in which the chlorine was evolved from manganese dioxide, salt, and sulphuric acid, and passed first through water, then through sulphuric acid, and finally over quicklime, when it passed in at the top of the bell-jar, leaving it by a tube passing to the bottom, thereby ensuring an even diffusion of the gas over the surface of the hydrate. A calcium chloride tube was placed beyond the bell-jar to prevent the absorption of moisture from the atmosphere by the substance. A slow and regular current of chlorine was maintained by means of a safety-tube.

From time to time the substance was turned over to expose fresh surfaces to the action of chlorine, which was allowed to pass until the bleaching powder no longer increased in weight. To remove adhering chlorine, a current of dry air was passed over the bleaching powder, which was then well powdered, transferred to a dry air-tight stoppered bottle, and kept in a cool dark place whilst undergoing analysis.

Six preparations were thus made—

I, II, III, and IV from Hydrate A.
V, from Hydrate B.
VI, from Hydrate C.

In determining firstly the relation of the molecules

$$Ca(OCl)_2 : CaCl_2 : Ca(OH),$$

the following method of analysis was adopted.

The total lime was determined by dissolving the substance in hydrochloric acid, precipitating the calcium as oxalate, and weighing as lime.

The total chlorine was estimated by first boiling the substance with ammonia (any calcium hypochlorite being thus converted into chloride), and the chlorine weighed as silver chloride.

Bunsen's method was adopted for the estimating of the available chlorine.

To estimate the free hydrate or any elements of hydrate that might be present, the bleaching powder was boiled with ammonia, whereby if Odling's formula is correct, the bleaching compound should be converted into calcium chloride, any calcium hydrate remaining unaltered, whilst according to Stahlschmidt's view, the following reaction should occur:—

$$3[2Ca\begin{cases} OCl \\ OH \end{cases} + CaCl_2] + 4NH_4HO = 6CaCl_2 + 3Ca(OH)_2 + 4N + 10H_2O,$$

the equivalent of calcium hydrate present being set free. The solution was then evaporated to dryness and the residue digested with alcohol (distilled over quicklime) for two hours at 70° C., which dissolved all the calcium chloride; the insoluble residue was collected, washed with alcohol, and weighed.

In three cases the water was determined by igniting the substance with lead oxide, and weighing the water collected in a calcium chloride tube.

From these data the values of $Ca(OCl)_2 : CaCl_2 : Ca(OH)_2$ can be calculated.

(1) Half the available chlorine = the actual amount of chlorine present combined with oxygen.
(2) The total chlorine $-\frac{1}{2}$ the available chlorine = chlorine present not combined with oxygen.
(3) Total CaO − free CaO = CaO combined with (1) and (2).

According to Stahlschmidt's formula therefore, in the strongest bleaching powder that can be prepared, the proportion of (1 + 2 + 3) to free lime cannot be greater than 2 : 1.

In every analysis the total chlorine was always slightly greater than double the actual oxidising chlorine, exactly which theory requires it to be. The difference between these quantities was always taken to be due to the presence of free calcium chloride consequent on the decomposition of some of the *bleaching compound*. In calculating the results, allowance was always made for the amount of CaO equivalent to this excess.

The results of analysis of the six samples of bleaching powder are tabulated below.

Preparation.	I.			II.		III.		IV.		V.		VI.
Total CaO.	1	2	3	1	2	1	2	1	2	1	2	1
Weight taken	0·2785	0·2610	0·3380	0·1717	0·350	0·3055	0·3200	0·4235	0·2735	0·2735	0·254	0·1870
CaO obtained	0·1125	0·1065	0·1485	0·071	0·1445	0·1265	0·1320	0·1606	0·1040	0·1145	0·1065	0·0765
Per cent. CaO	40·39	40·80	41·8	41·59	41·28	41·4	41·25	37·66	37·72	41·86	41·93	40·9
Mean	40·99			41·43		41·23		37·69		41·89		40·9
Free CaO.												
Weight taken	0·744	0·552	—	0·292	0·369	0·3365	0·508	0·4275	—	1·2805	—	0·374
CaO obtained	0·0987	0·068	—	0·037	0·046	0·033	0·049	0·047	—	0·1290	—	0·0520
Per cent. CaO	11·81	12·31	—	12·67	12·46	9·80	9·64	10·99	—	10·07	—	13·90
Mean	12·06			12·56		9·72		10·99		10·07		13·90
Total Chlorine.												
Weight taken	0·2115	0·204	0·202	0·1717	0·2526	0·339	0·3275	0·2915	0·386	0·3775	—	0·226
AgCl obtained	0·3255	0·2972	0·2985	0·244	0·3845	0·549	0·537	0·4115	0·545	0·6058	—	0·3225
Ag obtained	0·006	0·0063	0·0055	0·011	0·0165	0·006	0·005	0·009	0·004	0·0125	—	0·009
Per cent. Cl	38·6	37·06	37·08	37·46	37·87	40·64	41·03	35·9	35·2	40·75	—	36·6
Mean	37·58			37·66		40·83		35·55		40·75		36·6

Preparation.	I.	II.		III.		
Available Cl.						
Weight taken dilute to 100 c.c.	0·846	0·354	0·3275	1·462	0·723	0·905
Number of c.c. As_2O_3 solution required by 25 c.c.	20·4	8·00	7·4	37·75	17·8	23·00
1 c.c. As_2O_3 = gram Cl.	0·0032687	—	—	—	—	—
Per cent. available Cl	32·61	32·28	32·32	36·88	36·56	36·32
Mean	32·61	32·3		36·58		
Actual oxidising Cl	16·355	16·15		18·29		
Water.						
Weight taken	—	—	—	—	—	—
H_2O obtained	—	—	—	—	—	—
Per cent. H_2O	—	—	—	—	—	—
Mean	—	—	—	—	—	—

Preparation.	IV.			V.		VI.		
Available Cl.								
Weight taken dilute to 100 c.c.	0·9835	0·874	—	0·666	0·7432	1·4775	1·596	—
Number of c.c. As_2O_3 solution required by 25 c.c.	21·5	19·5	—	17·6	14·15	34·5	37·25	—
1 c.c. As_2O_3 = gram Cl	0·003776	—	—	—	—	—	—	—
Per cent. available Cl	33·12	32·71	—	39·8	39·1	34·9	35·25	—
Mean	33·41			39·35		35·07		
Actual oxidising Cl	16·755			19·675		17·535		
Water.								
Weight taken	0·4455	0·3615	0·7995	0·63	0·8658	0·9475	0·884	1·401
H_2O obtained	0·121	0·0995	0·2225	0·1130	0·1500	0 217	0·2000	0·3200
Per cent. H_2O	27·1	27·5	27·51	17·03	17·34	22·9	22·6	22·83
Mean	27·33			17·63		22·78		

A complete analysis :—

		I.	II.	III.	IV.	V.	VI.
a	CaO	40·99	41·43	41·23	37·69	41·89	40·9
b	Total Cl.....	37·58	37·66	40·83	35·55	40·75	36·6
	H_2O	—	—	—	27·33	17·63	22·78
					100·77	100·27	100·28
d	Free CaO	12·06	12·56	9·72	10·99	10·07	13·90
c	Actual oxidising Chlorine	16·355	16·15	18·29	16·755	19·675	17·535

If total CaO = *a*,
,, chlorine = *b*, and
actual oxidising chlorine = *c*,
then $2c$ = total chlorine entering into the composition of bleaching powder according to any of the formulæ quoted. $b - 2c$ = chlorine as $CaCl_2$ consequent on decomposition of some of the bleaching compound.

And $(b - 2c) \times \frac{56}{71}$ = CaO equivalent to $(b - 2c)$Cl.

Again if d = free CaO,
then $a - \{(b - 2c) \times \frac{56}{71} + d\}$ = CaO united with $2c$Cl. This is represented by ϵ.

	$b-2c$.	$(b-2c) \times \frac{56}{71}$.	$a - \left\{(b - 2c) \times \frac{56}{71} + d\right\} = \epsilon$.
I	4·97	3·92	24·01
II	5·34	4·18	24·79
III	4·25	3·35	28·16
IV	2·14	1·68	25·02
V	1·40	1·17	30·69
VI	1·53	1·20	25·80

$\frac{\epsilon}{56} : \frac{2c}{35{\cdot}5}$ = the molecular proportion of lime combined with oxidising and non-oxidising chlorine, to the total amount of these quantities :—

	$\frac{\epsilon}{56}$	:	$\frac{2c}{35{\cdot}5}$	CaO	:	Cl.
I.	0·43		0·91	1	:	2·1
II.	0·44		0·90	1	:	2·0
III.	0·50		1·03	1	:	2·06
IV.	0·447		0·94	1	:	2·1
V.	0·53		1·10	1	:	2·07
VI.	0·46		0·98	1	:	2·10

It is evident from this, therefore, that bleaching powder contains the elements of calcium hypochlorite and calcium chloride in equal molecular proportions. This being determined, the quantities of these two bodies corresponding to the values of c obtained, may be calculated for each sample and their relation to the quantity of hydrate.

	$Ca(OCl_2)$.	$CaCl_2$.	$Ca(OH)_2 = (OCl)_2 + H_2O$.	$\frac{Ca(OCl)_2}{143.}$	$\frac{CaCl_2}{111.}$	$\frac{Ca(OH)_2}{74.}$	$Ca(OCl)_2$	: $CaCl_2$	: $Ca(OH)_2$.
I.	32·04	24·56	15·93	0·223	0·222	0·215	1·00	1·00	1·00
II.	32·14	24·95	16·51	0·224	0·224	0·223	1·00	1·00	1·00
III.	35·45	28·29	12·86	0·255	0·255	0·173	1·5	1·5	1·00
IV.	32·90	25·53	17·99	0·23	0·23	0·241	1·00	1·00	1·00
V.	39·44	30·60	13·30	0·276	0·276	0·18	1·53	1·53	1·00
VI.	34·27	26·60	13·36	0·239	0·239	0·248	1·00	1·00	1·00

The formulæ required are therefore—

		Per cent. $Ca(HO_2)$ from above numbers.
I.	$Ca(OCl)_2 + CaCl_2 + Ca(OH)_2$	21·95
II.	„ „ „	22·41
III.	$3Ca(OCl)_2 + 3CaCl_2 + 2Ca(OH)_2$....	16·70
IV.	$Ca(OCl)_2 + CaCl_2 + Ca(OH)_2$	23·55
V.	$3Ca(OCl)_2 + 3CaCl_2 + 2Ca(OH)$....	15·25
VI.	$Ca(OCl)_2 + CaCl_2 + Ca(OH)_2$	23·19

$Ca(OCl)_2 + CaCl_2 + Ca(OH)_2$ requires 22·56 per cent. $Ca(OH)_2$.
$3Ca(OCl)_2 + 3CaCl_2 + 2Ca(OH)$ „ 16·26 per cent. $Ca(OH)_2$.

These results show that it is possible to prepare bleaching powder containing $Ca(OCl)_2 + CaCl_2 + Ca(OH)_2$ in greater proportion than that required by Stahlschmidt's formula, but still two-thirds of the cases fulfil the conditions required, and therefore these results cannot be considered as absolutely conclusive. They, however, distinctly show that the proportion is variable, and hence the improbability of Stahlschmidt's conclusion.

Further evidence was brought to bear on this point in the results derived from endeavours made to rid the bleaching compound of free calcium chloride, supposing such to be present in the bleaching powder. This was carried out by rapidly washing the bleaching powder several times with alcohol distilled over lime, which would dissolve the calcium chloride, and leave behind the *bleaching compound*, together with calcium hydrate. It was only necessary to determine in the residue the

Total CaO,
Free CaO,
Total chlorine, and
Available chlorine,

to obtain the necessary data for arriving at the true constitution of the bleaching compound.

It may here be mentioned that some decomposition took place when the bleaching powder was treated with alcohol, but as this would result in the formation of calcium chloride soluble in alcohol and lime, which would be directly estimated, it did not affect the results. An unweighed quantity of bleaching powder was washed six times with alcohol, the last washings being tested for calcium chloride, and found to contain only slight traces of chlorine, and in no case did the filtrate liberate iodine from potassium iodide, hence no hypochlorite was present. The undried residue was dissolved in water (it was ascertained that considerable decomposition ensued when the residue was dried over sulphuric acid previous to dissolving in water), and the volume was made up to 100 c.c. Preparations V and VI were used in these experiments, of which two were made in each case, with the following results:—

Preparation.	VI.		V.	
Total CaO.	1	2	1	2
Vol. taken	10·0 c.c.	10·0 c.c.	10·0 c.c.	10·0 c.c.
CaO obtained.....	0·0405	0·0440	0·069	0·0700
CaO in 100 c.c.	0·405	0·44	0·69	0·70
Free CaO.				
Vol. taken	10·0 c.c.	10·0 c.c.	10·0 c.c.	10·0 c.c.
CaO obtained.....	0·023	0·023	0·031	0·033
CaO in 100 c.c.	0·23	0·23	0·31	0·33

Preparation.	VI.		V.	
Total Cl.				
Vol. taken	10·0 c.c.	10·0 c.c.	10·0 c.c.	10·0 c.c.
Vol. $AgNO_3$ required, 1 c.c. = 0·001 gram Cl	19·5	25·4	AgCl 0·188 Ag 0·010	0·208 0·004
Cl obtained	0·0195	0·0254	0·0498	0·0513
Cl in 100 c.c.	0·195	0·254	0·498	0·513
Available Cl.				
Vol. taken	10·0 c.c.	10·0 c.c.	10·0 c.c.	10·0 c.c.
Vol. As_2O_3 solution required, 1 c.c. = 0·00003684 Cl	49·0 c.c.	68·0 c.c.	136·0 c.c.	139·0 c.c.
Cl obtained	0·0181	0·0248	0·0497	0·0517
Cl in 100 c.c.	0·181	0·248	0·497	0·517
Actual oxidising Cl	0·0905	0·124	0·2485	0·2585
Summary.	100 c.c. of each solution contains—			
Total CaO (a)	0·405	0·44	0·690	0·700
Total Cl (b)	0·195	0·254	0·498	0·513
Actual oxidising Cl = c	0·0905	0·124	0·2485	0·2585
Free CaO = d	0·230	0·230	0·310	0·330

Then, as before—

	VI.		V.	
	1	2	1	2
$b - 2c$ = Cl as $CaCl_2$ due to decomposition	0·014	0·006	0	0
$(b - 2c) \times \frac{56}{74}$ = CaO equivalent to above	0·011	0·044	0	0
$a - \left\{ (b-2c)\frac{56}{74} + d \right\}$ = CaO in bleaching compound = ϵ	0·164	0·206	0·38	0·37

From these data we arrive at the following conclusions:—

Preparation.	VI.		V.	
	1	2	1	2
(1.) $\frac{\text{Actual oxidising Cl}}{\text{Total Chlorine}}$	$\frac{1}{2\cdot01}$	$\frac{1}{2\cdot01}$	$\frac{1}{1}$	$\frac{1}{1\cdot98}$
$\frac{\epsilon}{56}$	0·0029	0·00367	0·00678	0·0066
$\frac{2c}{35\cdot5}$	0·0051	0·00701	0·014	0·0145
$\frac{\text{CaO in bleaching compound}}{\text{Total Cl in bleaching compound}}$	$\frac{1}{1\cdot8}$	$\frac{1}{1\cdot9}$	$\frac{1}{2\cdot09}$	$\frac{1}{2\cdot2}$
$\frac{\text{CaO in bleaching compound}}{\text{Actual oxidising Cl in compound}}$	$\frac{1}{0\cdot9}$	$\frac{1}{0\cdot95}$	$\frac{1}{1\cdot045}$	$\frac{1}{1\cdot1}$

The results therefore prove conclusively that in the *bleaching compound*

The CaO : Total Cl :: 1 : 2.
CaO : Actual oxidising Cl :: 1 : 1.
Actual oxidising Cl : Total Cl :: 1 : 2.

By examining the formulæ for bleaching powder proposed by Gay-Lussac and Stahlschmidt and Odling, it appears plainly that if Gay-Lussac's represents the compound, the residue, after treatment with alcohol, will consist of $Ca(OCl)_2$, in which

The CaO : Total Cl :: 1 : 2.
CaO : Oxidising Cl :: 1 : 2.
Actual oxidising Cl : Total Cl = 1 : 1.

According to Stahlschmidt's view, the residue would consist of $Ca\left\{\begin{matrix}OCl\\OH\end{matrix}\right.$, and here we have the proportions—

CaO : Total Cl :: 1 : 1.
CaO : Oxidising Cl :: 1 : 1.
Actual oxidising Cl : Total Cl :: 1 : 1.

whereas Odling's formula would leave the residue of the composition $Ca\left\{\begin{matrix}OCl\\Cl\end{matrix}\right.$, giving the proportions—

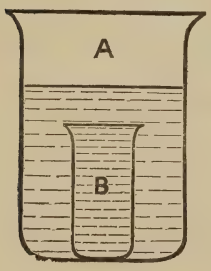
CaO : Total Cl = 1 : 2.
CaO : Actual oxidising chlorine = 1 : 1.
Actual oxidising Cl : Total Cl = 1 : 2.

each of which conditions is fulfilled by the results detailed above.

It may therefore be safely concluded that Odling's formula represents the constitution of the *bleaching compound* in bleaching powder, and these results also show that bleaching powder contains excess of free $Ca(OH)_2$, which does not enter into the bleaching compound.

Action of Water on Bleaching Powder.

The preparation of calcium hypochlorite from bleaching powder, by Kingzett (this Journal, 1875, 404), leaves little doubt that bleaching powder in solution contains calcium hypochlorite and calcium chloride, but after the above results had been obtained it appeared interesting to determine directly the decomposition of the substance by water. It was thought probable that diffusion might throw some light on the subject, for if a solution of bleaching powder contains the body $Ca\begin{cases} OCl \\ Cl \end{cases}$, it may be assumed that on subjecting such a solution to diffusion, the proportion of total chlorine to actual oxidising chlorine (2 : 1) will be the same in the diffusate and in the residue and original substance; but, on the other hand, taking for granted the decomposition of the compound $Ca\begin{cases} OCl \\ Cl \end{cases}$ into calcium hypochlorite and calcium chloride, it is natural to suppose that calcium chloride will diffuse more rapidly than calcium hypochlorite, and such being the case, the proportion of total chlorine to actual chlorine in the residue will be less than in the diffusate and original substance. The experiments were carried out as follows:—



A given weight of bleaching powder was dissolved in a weighed quantity of water, such that when placed in the beaker B, the solution should fill the latter to within half an inch of the top, the beaker being filled up with distilled water. The beaker B was surrounded with a measured volume of distilled water, and in each case left at rest in the dark for 25 days.

After that time the whole of the surrounding solution in A was carefully siphoned off without shaking, and the volume of the residue in B made up to 100 c.c.

The ratio of available to total chlorine was determined in both solutions.

The bleaching powder used was Sample VI.

I. 5·0195 grams bleaching powder were dissolved in 75 grams water.
Strength of the solution = 6·2 per cent.
Volume of surrounding solution = 300 c.c.

	Diffusate. Total vol. = 300 c.c.		Residue. Total vol. = 100 c.c.	
Available Chlorine.				
Vol. taken.....	25·0 c.c.	—	10·0 c.c.	—
Vol. As_2O_3 required ..	16·25	—	28·8	—
1 c.c. As_2O_3.....	0·003648 Cl	—	0·003648 Cl	—
Available Cl.[a].....	0·0538	—	0·10506	—
Actual oxidising Cl. in total vol.....	0·35628	—	0·5253	—
Total Chlorine.				
Vol. taken.....	10·0 c.c.	—	10·0 c.c.	10·0 c.c.
Vol. $AgNO_3$ required..	28·9	AgCl obtained	0·4075	0·400
1 c.c. $AgNO_3$ = 0·001 grm. Cl.	—	Ag „	0·0050	0·0050
Total Cl.....	0·0289	—	0·1024	0·1009
Cl in total vol.....	0·867	(mean)	1·016	

II. Weight of bleaching powder taken = 4·639 grams, dissolved in 75 grams water.
Strength of solution = 5·8 per cent.
Volume of surrounding solution = 400 c.c.

	Diffusate. Total vol. = 300 c.c.		Residue. Total vol. = 100 c.c.	
Available Chlorine.				
Vol. taken	25·0 c.c.	—	10·0 c.c.	—
Vol. As_2O_3 required ..	11·25	—	26·3	—
1 c.c. As_2O_3	0·003648	—	—	—
Available chlorine....	0·4122	—	0·09712	—
Actual oxidising Cl in total vol.....	0·32975	—	0·4856	—
Total Chlorine.				
Vol. taken.....	10·0 c.c.	—	10·0 c.c.	10·0 c.c.
Vol. $AgNO_3$ required .	20·7	AgCl obtained	0·359	0·3200
1 c.c. $AgNO_3$ = 0·001 grm. Cl.	—	Ag „	0·013	0·0478
Total chlorine.....	0·0207	—	0·0933	0·0927
Cl in total vol.	0·827	(mean)	0·930	

By comparing the quantities of total and actual oxidising chlorine present in the various solutions, as above determined, with the quantity of each present in the weight of bleaching powder taken, the following result is obtained :—

I.

	Original substance.	Diffusate.	Residue.
Actual weight of bleaching Cl.....	0·886	0·3567	0·5253
Chlorine as $CaCl_2$ = total Cl—actual weight of oxidising chlorine	0·957	0·5108	0·4907

II.

Oxidising chlorine.....	0·8134	0·3297	0·4856
Chlorine as $CaCl_2$	0·8844	0·4483	0·4444

The amount of oxidising chlorine is actually greater than that of the chlorine as $CaCl_2$ in the residue, but considerably less than in the diffusate, whereas they are almost equal in the original substance, consequently the substances have diffused unequally, and this result is due to the decomposition of the bleaching compound.

If the quantities of calcium chloride and calcium hypochlorite corresponding to the above quantities of chlorine be calculated, it becomes still more apparent that decomposition has taken place.

	Original substance.	Diffusate.	Residue.
I. $CaCl_2$.....	1·496	0·7985	0·7812
$Ca(OCl)_2$	1·772	0·7173	1·058
II. $CaCl_2$.....	1·382	0·777	0·694
$Ca(OCl)_2$	1·638	0·664	0·978

Taking the proportion of these quantities—

I. $CaCl_2 : Ca(OCl)_2$	1 : 1·17	1 : 0·898	1 : 1·34
II. $CaCl_2 : Ca(OCl)_2$	1 : 1·18	1 : 0·84	1 : 1·41

and it is seen that the proportion which is greater than unity in the cases of the original substance residue becomes less than unity in the case of the diffusate. These numbers fully confirm Kingzett's results, and it is now established beyond doubt that the aqueous solution of bleaching powder contains calcium chloride and calcium hypochloride.

The conclusions to be drawn from these results are—

(1.) That the excess of the hydrate present in bleaching powder is not a constant quantity.

(2.) That the formula of the bleaching compound is $Ca\left\{\begin{matrix}OCl\\Cl\end{matrix}\right.$.

(3.) That by the action of water this compound undergoes the following decomposition:—

$$2Ca\left\{\begin{matrix}OCl\\Cl\end{matrix}\right. = Ca(OCl)_2 + CaCl_2.$$

LX.—*Researches on Secondary and Tertiary Azo-Compounds.* No. I.

By Raphael Meldola.

Introduction.

The series of compounds containing the diazo-group —N=N—, first discovered by Griess, have of late years largely occupied the attention of chemists, both on account of their great scientific interest and their technical importance as colouring matters. The bodies of this class have, as is well known, supplied to commerce a splendid series of dye-stuffs, ranging from brilliant yellow and orange, through various shades of scarlet and brown, to bluish-violet. The discovery of these "diazo-colours" has indeed created quite new branches of the tinctorial industry, and the utilisation of those portions of coal-tar which, like the higher homologues of benzene and naphthalene, were at one time waste products, but which are now consumed in enormous quantities, is almost entirely due to their introduction.

Up to the present time attention has chiefly been directed to the investigation of those bodies constructed on the type of azobenzene:—

$$C_6H_5—N=N—C_6H_5,$$

the phenyl (or naphthyl) residues on one or both sides of the diazo-group containing acid or basic substituents, such as HO, HSO_3, COOH, NH_2, $N(CH_3)_2$, $C_6H_4.NH.C_6H_5$, &c. Adopting the nomenclature proposed by Wallach (*Ber.*, 1882, 2812), the compounds of this class may conveniently be termed *primary* azo-compounds.

The *secondary* azo-compounds containing the —N=N— group twice, fall under two distinct types:—

(I.) Those in which the diazo-groups are both in the phenol residue; represented by Griess's "phenol-bidiazobenzene" (*Ber.*, 1876, 628)—

$$\left.\begin{matrix}C_6H_5—N=N\\C_6H_5—N=N\end{matrix}\right\rangle C_6H_3(HO),$$

and by Weselsky and Benedikt's phloroglucinol-bidiazobenzene (*Ber.*, 1879, 226), which has the formula—

$$\left.\begin{matrix}C_6H_5—N=N\\C_6H_5—N=N\end{matrix}\right\rangle C_6H(HO)_3.$$

The bodies of this class have recently formed the subject of in-

teresting papers by Wallach and others (*Ber.*, 1882, 22; 2814, 2825, and 3020).

(II.) The azo-compounds of the second class may be regarded as being constituted on the type of azo-azobenzene—

$$C_6H_5—N{=}N—C_6H_4—N{=}N—C_6H_5,$$

and are represented by Caro and Schraube's oxyazo-azobenzene (*Ber.*, 1877, 2230)—

$$C_6H_5—N{=}N—C_6H_4—N{=}N—C_6H_4(HO),$$

or by the corresponding β-naphthol-compound described by Nietzki (*Ber.*, 1880, 1838)—

$$C_6H_5—N{=}N—C_6H_4—N{=}N—C_{10}H_6(HO)\beta.$$

To this class belong the well-known and important commercial products, the "Biebrich" * and "Croceine"† scarlets, &c.

The compounds of the first class are formed by the successive introduction of two similar or dissimilar diazotised nuclei into a phenol (Wallach's "disazo-compounds").‡

The bodies of the second type, to which I have confined my investigations, have hitherto been prepared by two methods:—

(1.) By the action of a diazotised amidoazo-compound (or its sulphonic acid) upon a phenol or substituted phenol.

(2.) By the neutralisation of one amido-group in an aromatic diamine by an acid radicle (acetyl), the diazotising of the remaining amido-group, and the copulation of the diazo-compound thus formed with a phenol. The acid radicle is then eliminated, and the restored amido-group diazotised and copulated with a second phenol residue (Wallach, *Ber.*, 1882, 2825).

Having for some years past been interested in the technical pro-

* Nietzki, *Ber.*, 1880, pp. 800 and 1838; W. v. Miller, *ibid.*, pp. 542, 803, and 980; Léo Vignan and J. B. Boasson, *ibid.*, p. 1060; Grässler, *Germ. pat.*, No. 38919, 1880; Krügener, *Germ. pat.*, No. 36792, 1880; also F. Bayer and Co. (Amidonaphthalene-tetrazobenzene-sulphonic acids), *Germ. pat.*, No. 20000, 1882; Farbw. vorm. Meister, Lucius and Brüning, *Germ. pat.*, No. 22010, 1882.

† F. Bayer and Co., *Germ. pat.*, No. 18027, 1881.

‡ Diamidoazo-compounds of the Chrysoïdine class appear also capable of being converted into disazo-compounds by the introduction of a second diazotised radicle. See *Germ. pat.*, No. 22714 of the *Aktiengesellschaft für Anilinfabrikation*, 1883.

[Since writing the above note a paper has just been published by Dr. Griess (*Ber.*, 1883, p. 2028), in which are described several secondary azo-compounds of the class referred to, viz., $\begin{matrix}R—N{=}N\\R—N{=}N\end{matrix}\!>\!R(NH_2)_2$, as well as tertiary compounds of the mixed type $R—N{=}N—R—N{=}N—R\!<\!\begin{matrix}N{=}N—R\\(NH_2)_2\end{matrix}$.

duction of azo colouring-matters, I commenced last year a series of experiments, having for their object the extension of our knowledge of the secondary azo-compounds and the production of the hitherto imperfectly known tertiary compounds. It occurred to me that the desired results could be most simply arrived at by starting from a nitro-derivative of an amidoazo-compound—

$$NO_2.R—N=N—R.NH_2.$$

Such a body when diazotised and united with a phenol residue (Ph) would give rise to the formation of a secondary nitroazo-compound of the type—

$$NO_2.R—N=N—R—N=N—Ph.$$

A body of the above type would, if it were possible to reduce the nitro-group without at the same time splitting up the azo-groups, give by a repetition of the foregoing processes a tertiary compound of the formula—

$$Ph—N=N—R—N=N—R—N=N—Ph.$$

The same result would also be obtained by first reducing the nitro-amidoazo-body so as to obtain a diamidoazo-compound of the type—

$$NH_2.R—N=N—R.NH_2,$$

then diazotising the two amido-groups simultaneously, and finally combining the product with 2 mols. of a phenol. As the result of the present investigations, I have thus far found that this last process alone works in a satisfactory manner.

Up to the present time, nitro-derivatives of the amidoazo-compounds have been but little studied, and experiments were therefore in the first place directed to the production of some of these bodies, the most obvious method that suggested itself being the action of diazotised nitroamido-derivatives of aromatic hydrocarbons upon primary monamines. Thus, in the case of the benzene series:—

$$NO_2.C_nH_{2n-8}.N_2.Cl + C_nH_{2n-7}.NH_2 = NO_2.C_nH_{2n-8}.N_2.C_nH_{2n-8}.NH_2 + HCl.$$

The experiments herein recorded were all made with paranitraniline.*

* To prepare this compound in large quantities, the following method was adopted:—Equal volumes of nitric acid (sp. gr. 1·420) and strong sulphuric acid are mixed and well cooled. Acetanilide is then gradually introduced and the mixture agitated after each addition so as to dissolve the solid crystals. When no more acetanilide is taken up, the solution is left at rest for about half an hour, and kept thoroughly cooled during this time. The contents of the flask are then

Action of Diazotised Paranitraniline upon Primary Monamines.

I. *Action upon Metaxylidine.*

Some preliminary experiments having shown that the most decided results were given by the action of diazoparanitrobenzene salts upon *meta*-monamines, such as metatoluidine or metaxylidine, the last-named substance was employed. Throughout these investigations the following method of diazotising was adopted:—The nitraniline is powdered and mixed with a small quantity of water, and then strong hydrochloric acid is added till the crystals just dissolve. The theoretical quantity of sodium nitrite dissolved in water is then slowly added, and the mixed solutions kept thoroughly cool. The diazo-compound is immediately formed, and by this means practically the whole of the nitraniline is converted, whereas by departing from this method, a considerable quantity of the nitraniline is apt to be converted into an insoluble yellow compound, probably a dinitroamidoazobenzene.

Paranitrobenzene-azoamidometaxylene, $NO_2.C_6H_4.N_2.C_8H_8.NH_2$, is formed by filtering a solution of paranitrodiazobenzene chloride (1 mol.) into an alcoholic solution of metaxylidine hydrochloride (1 mol.). A bulky reddish precipitate soon separates, causing the contents of the beaker to become semi-solid. This precipitate consists of the diazo-compound $NO_2.C_6H_4.N_2.NH.C_8H_9$, which, on standing for a few hours, becomes converted into the isomeric azo-compound, the latter forming a bright scarlet hydrochloride. This salt was collected, washed with alcohol acidulated with hydrochloric acid, and finally with water. Ammonia liberates the base as a brown substance which crystallises from dilute alcohol in brick-red needles, having a melting point of 141° C. The base is readily soluble with an orange colour in alcohol, acetone, benzene, and chloroform. It dissolves also with an orange colour in strong sulphuric acid. A platinum salt was formed by adding $PtCl_4$ and HCl to a dilute alcoholic solution of the base. The salt separates out in minute scales having a metallic green reflection.

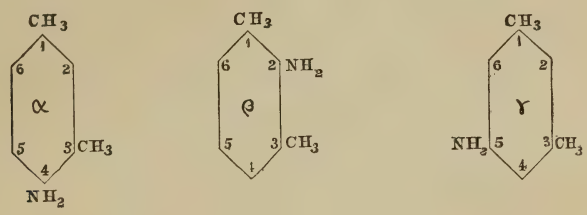
0·2314 gram gave 0·477 gram Pt.

Theory for $2(C_6H_4<^{NO_2}_{N_2.C_8H_8.NH_2,HCl})PtCl_4$.		Found.
Pt	20·72 per cent.	20·61

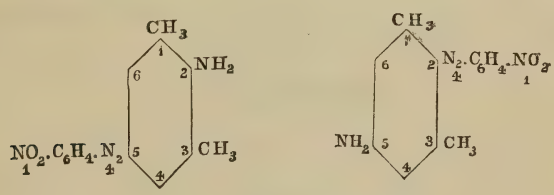
stirred into a large bulk of cold water, and the nitro-compound is collected, washed, and crystallised from boiling water. On saponification by boiling NaHO solution, paranitraniline separates out on cooling. By following this method but a very small quantity of orthonitraniline appears to be produced, and one or two crystallisations from water furnish the para-compound in a state of perfect purity.

The salts of this base are very insoluble in alcohol, and separate out in beautiful red needles having a violet reflection when HCl, H_2SO_4, or HNO_3, is added to a hot alcoholic solution. With respect to the constitution of this substance, the following observations may be offered:—

The three known metaxylidines possess the constitutional formulæ:—



When a diazotised radicle combines with an amine, the N_2-group always takes up the para-position with respect to the amido-group. This is shown by the circumstance that diazotised paranitraniline gives no definite compound with paratoluidine, whilst with orthotoluidine it gives a small yield, and with metatoluidine a rich yield of an azo-compound. All three metaxylidines occur in the xylidine from coal-tar xylene, but the α-modification can take no part in the present reaction, and the body described is therefore most probably a mixture of the two modifications:—



By complete reduction both these compounds would give rise to paradiamidobenzene and the *same* diamidoxylene, so that the relative positions of the NH_2 and $-N_2.C_6H_4.NO_2$-groups with respect to the CH_3-groups, cannot be determined by this method. The formula of the new compound may thus be written:—

$$\underset{1}{NO_2}.C_6H_4.\underset{4}{N}{=}\underset{(2\,\&\,5)}{N}.C_6H_2.\underset{3}{CH_3}.\underset{1}{CH_3}.\underset{(5\,\&\,2)}{NH_2}.$$

II. *Action of Diazoparanitrobenzene upon α-Naphthylamine.*

Paranitrobenzene-azoamido-α-naphthalene,

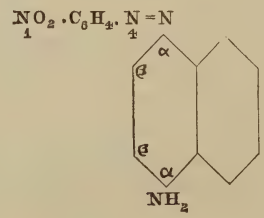
$$NO_2.C_6H_4.N{=}N.C_{10}H_6.NH_2,$$

was prepared in precisely the same manner as the xylene compound. On mixing the solutions a deep crimson colour is developed, and a bulky brown precipitate forms. The substance was purified by washing with alcohol acidulated with HCl, and finally with hot water. By treatment with ammonia the base was obtained as a brown substance, somewhat difficultly soluble in boiling alcohol. The solution is of a fine crimson colour, and minute needles are deposited on cooling. The base dissolves in benzene and its homologues with an orange colour, and crystallises therefrom in brown glistening needles. A specimen crystallised from toluene had a melting point of 252°. On adding hydrochloric acid to a hot alcoholic solution, the hydrochloride crystallises out in hair-like needles, having a faint violet shimmer. The base dissolves in strong sulphuric acid with a violet colour. The platinum salt was obtained as a violet non-crystalline precipitate on adding HCl and $PtCl_4$ to hot solution of the base in alcohol.

0·1052 gram gave 0·0205 gram Pt.

Theory for $2(C_6H_4{<}^{NO_2}_{N_2.C_{10}H_6.NH_2,HCl})PtCl_4$.	Found.
Pt ..... 19·81 per cent.	19·48

By complete reduction this substance is resolved into paraphenylene-diamine, and a naphthylene diamine yielding α-naphthoquinone on oxidation. Its constitution is therefore :—



III. *Action of Diazoparanitrobenzene upon β-Napthylamine.*

Paranitrobenzene-azoamido-β-naphthalene,

$$NO_2.C_6H_4.N{=}N.C_{10}H_6.NH_2.$$

This body was prepared in a similar manner to the α-compound, but it was found more advantageous in this case to work with an aqueous instead of an alcoholic solution of the naphthylamine hydrochloride, as

the salts of the nitroamidoazo-β-compound are readily soluble in alcohol, and do not separate out on dilution in a convenient state for purification. Great care must also be taken to avoid an excess of sodium nitrite in diazotising the paranitraniline; otherwise amidoazo-β-naphthalene is apt to be formed, and is most difficult to separate from the substance required.

On mixing the solutions containing the theoretical quantities of paranitrodiazobenzene and β-naphthylamine hydrochloride, a bronzy-looking precipitate immediately separates. This was collected, washed with water, basified and dried. On dissolving in boiling alcohol a red solution was obtained, which on cooling deposited magnificent needles, having a bright metallic golden lustre and melting at 180° C. The base possesses the following properties:—It dissolves in alcohol, acetone, and chloroform, with a red colour, whilst its solutions in benzene, toluene, &c., are orange-coloured. It dissolves in strong sulphuric acid with a violet colour, becoming red on dilution with water. The salts of the base, unlike those of the corresponding α-compound, are readily soluble in alcohol, so that nothing separates out when hydrochloric acid is added to the alcoholic solution. The platinum salt was obtained as a reddish-brown amorphous powder, by adding $PtCl_4$ to a strong alcoholic solution of the hydrochloride.

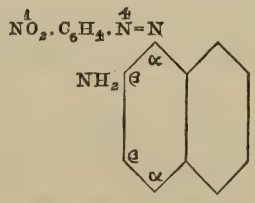
0·1713 gram gave 0·0335 gram Pt.

	Theory.	Found.
Pt	19·81 per cent.	19·55

0·2319 gram burnt with CuO gave 38·4 c.c. N at 18·2°, and 752·3 mm. bar. = 0·0438 gram N.

Theory for $C_6H_4<^{NO_2}_{N_2.C_{10}H_6.NH_2}$.	Found.
N ..... 19·17 per cent.	18·88

I have not yet succeeded in obtaining from this substance by complete reduction the naphthylenediamine giving β-naphthoquinone on oxidation. Its constitution is, however, most probably*—



* The extreme stability of the substance is opposed to the idea that we may here have the isomeric diazo-compound, $C_6H_4<^{NO_2}_{N=N-N<^{H}_{C_{10}H_7\beta}}$.

The behaviour of this body both on reduction and when acted upon by HNO_2, as will be seen hereafter, is in many ways remarkable, and I propose to make its investigation the subject of special study on some future occasion.

Reduction of the Nitroamidoazo-compounds.

Paraamidobenzene-azoamidometaxylene, $\underset{1}{NH_2}.C_6H_4.\underset{4}{N}{=}N.C_8H_8.NH_2$. — The nitroamidoazo-compound obtained by the action of paranitrodiazobenzene chloride upon metaxylidine was converted into a state most suitable for reduction by dissolving it in alcohol and stirring the solution into cold water. The bulky red semi-gelatinous precipitate was collected, washed with water till free from alcohol, and then warmed for some hours with ammonium sulphide. The colour of the precipitate gradually changes to yellow, and the diamido-base separates in a crystalline form. The latter was purified by crystallisation from boiling water, and was obtained in the form of beautiful golden-yellow scales melting at 163°. This base is extremely soluble in alcohol, benzene, and most solvents. Its solution in strong sulphuric acid is yellow, changing to orange on dilution. The solutions of the hydrochloride, sulphate, and nitrate are orange-coloured, and these salts are extremely soluble in water. By adding excess of acid the biacid salt is precipitated; thus on adding an excess of HCl to a solution of the hydrochloride, the salt, $C_6H_4{<}\overset{NH_2}{N_2.C_8H_8.NH_2,2HCl}$, separates out as a bulky brown non-crystalline precipitate. A platinum salt was precipitated as a brown amorphous powder by adding $PtCl_4$ to the aqueous solution of the hydrochloride.

0·0958 gram gave 0·0289 gram Pt.

Theory for $(C_6H_4{<}\overset{NH_2}{N_2.C_8H_8.NH_2})2HCl.PtCl_4$.	Found.
Pt ..... 30·21 per cent.	30·16

Paraamidobenzene-azoamido-α-naphthalene,

$$\underset{1}{NH_2}.C_6H_4.\underset{4}{N}{=}\underset{\alpha}{N}.C_{10}H_6\underset{\alpha}{NH_2},$$

was prepared in the same manner as the last compound. The brown gelatinous nitroamidoazo-body, on digestion with ammonium sulphide, became converted into a mass of ochreous needles, melting when dry at about 159—160°. The salts of this diamido-base dissolve readily in water, giving solutions of a magenta-like red; excess of acid precipitates the biacid salts. The base is readily soluble in alcohol, acetone, benzene, and chloroform. Its solution in strong sulphuric acid is of a

fine red colour. The platinum salt is similar in appearance, and was prepared in the same manner as the last.

0·1174 gram gave 0·0342 gram Pt.

Theory for $(C_6H_4<^{NH_2}_{N_2.C_{10}H_6.NH_2})2HCl.PtCl_4$.		Found.
Pt	29·27 per cent.	29·13

On acting upon an aqueous solution of the hydrochloride with zinc-dust complete reduction takes place, and the solution becomes colourless. The excess of zinc was filtered off, and ferric chloride added to the filtrate, which, on standing, deposited a brownish crystalline substance. The latter was collected, washed, boiled with water, and filtered. The filtrate on cooling deposited a mixture of small yellow and larger red needles, the two kinds of crystals being easily separable when dry. The melting points proved that the yellow crystals were benzoquinone and the red crystals α-naphthoquinone, thus establishing the constitutional formula previously assigned.

Reduction of Paranitrobenzene-azoamido-β-naphthalene.

It was not found possible to obtain this substance in a convenient form for reduction in an aqueous solution with ammonium sulphide, as the bronzy paste precipitated by water from an alcoholic solution soon becomes crystalline, and is then unacted upon by the reducing agent. Rapid reduction takes place, however, when ammonium sulphide is added to a cold alcoholic solution of the base. The colour of the solution immediately changes from red to yellow, and on pouring into water a bright orange precipitate is thrown out. This substance is not simply the diamidoazo-compound, but it appears to contain sulphur, and is readily fusible in boiling water. I propose to study this reaction in greater detail hereafter.

The diamidoazo-compounds described above are the first known members of a series of bases isomeric with the "chrysoïdine" series discovered by Dr. O. N. Witt. They differ from the latter in having the amido-groups in different aromatic nuclei:—

$R'—N{=}N—R'''(NH_2)_2$.	$NH_2.R''—N{=}N—R''.NH_2$.
Chrysoïdine series.	New series.

These new bases are yellow or orange dye-stuffs, and are best applied in a neutral or slightly alkaline bath. By the action of nitrous acid both amido-groups are readily diazotised, thus affording a means, as will be seen subsequently, of preparing a whole series of new tertiary azo-compounds.

Secondary Nitroazo-Compounds.

$$NO_2.R—N{=}N—R—N{=}N—Ph.$$

Nitrous acid acts readily upon paranitrobenzene-azoamidometaxylene, the amido-group becoming diazotised, and thus furnishing a starting point for the production of a series of secondary nitroazo-bodies. After various experiments the following method was adopted:—The theoretical amount of $NaNO_2$ dissolved in a small quantity of water, was added to the solution of the base in alcohol, and the mixture whilst kept thoroughly cooled acidulated with hydrochloric acid. The hydrochloride of the base is first precipitated, but this soon redissolves, and an orange-coloured solution of the tetrazo-salt is obtained. The latter was then poured with constant stirring into a cold aqueous solution containing the theoretical quantity of the phenol dissolved in an alkali. Of the various compounds thus obtained, the β-naphthol-body was alone studied in detail, as this was the only one that could be obtained easily in a state of purity by crystallisation.

Paranitrobenzene-azometaxylene-azo-β-naphthol,

$$C_6H_4{<}^{NO_2}_{N_2.C_8H_8.N_2.C_{10}H_6.HO\beta}.$$

On mixing the solutions of the tetrazo-chloride and sodium β-naphtholate in the manner above described a brown precipitate separated, which was collected, washed with water till the filtrate was no longer yellow, and dried. A green metallic powder was thus obtained, which was dissolved in boiling aniline, and the crimson solution on cooling deposited small brilliant metallic-green needles, which were collected, washed with alcohol, and dried. The aniline filtrate contained a small quantity of a substance apparently identical in all respects with the green needles, so that no soluble isomeride appears to be produced in this reaction. A specimen was purified for analysis by another crystallisation from toluene, in which solvent the substance dissolves at the boiling point with a crimson colour, and separates on cooling in green glistening scales having a fusing point of 278°.

I. 0·2745 gram gave 0·6816 gram CO_2 and 0·1202 gram H_2O.
II. 0·1387 gram gave 20 c.c. N at 19·3° and 755·4 mm. bar. = 0·0228 gram N.

	Theory for $C_{24}H_{19}N_5O_3$.	Found. I.	Found. II.
C	67·76	67·71	—
H	4·47	4·86	—
N	16·47	—	16·43

The substance is but very slightly soluble in alcohol or glacial acetic acid, even when boiled with these solvents. It dissolves somewhat more freely in boiling alcoholic potash, the solution being violet at first, but becoming red on standing. It is soluble in boiling nitrobenzene with a magenta-like red colour, and it gives a green colour in strong sulphuric acid, changing to violet on dilution. Fuming sulphuric acid (80 per cent. anhydride) converts it into a sulphonic acid having no particular tinctorial properties. Although this compound, like the nitroamidoazo-body from which it is derived, probably contains two isomeric modifications, the two isomerides, if present, differ to so small an extent in their degree of solubility and other properties that no separation could be effected. The constitutional formula may be written:—

$$\underset{1}{NO_2}.C_6H_4.\underset{4}{N}=\underset{(2\,\&\,5)}{N}.C_6H_2.\underset{3}{CH_3}.\underset{1}{CH_3}.\underset{(5\,\&\,2)}{N}=\underset{\alpha}{N}.C_{10}H_6.\underset{\beta}{HO}.$$

The secondary nitroazo-compounds represented by the present substance did not appear to furnish promising starting-points for the preparation of tertiary azo-compounds, since the nitro-group was not readily reducible, and even when reduced the resulting secondary amido-compound could not be diazotised. The following members of the series were not studied in much detail.

Paranitrobenzene-azometaxylene-azo-α-naphthol—

$$\underset{1}{NO_2}.C_6H_4.\underset{4}{N}=N.C_8H_8.\underset{\alpha}{N}=N.C_{10}H_6.\underset{\alpha}{HO}.$$

This body resembles the foregoing in its general characters, but is rather more soluble in alcohol, glacial acetic acid, &c. The solutions are redder than those of the β-naphthol-compound, but the substance is not readily crystallisable.

Paranitrobenzene-azo-metaxylene-azo-β-naphtholsulphonic acid—

$$\underset{1}{NO_2}.C_6H_4.\underset{4}{N}=N.C_8H_8.\underset{\alpha}{N}=N.C_{10}H_5.\underset{\beta}{HO}.\underset{\beta}{HSO_3}.$$

The ammonium salt of this acid was precipitated as a reddish gelatinous substance on mixing the solution of the tetrazo-salt with a solution of the ammonium salt of Schäffer's β-naphtholsulphonic acid, and adding ammonia. The salts of this acid are all very insoluble, and from an acid bath dye silk and wool of a claret-red.

The corresponding compound from α-naphtholsulphonic acid is similar to the above, but dyes of a reddish-brown shade.

Paranitrobenzene-azometaxylene-azophenol—

$$\underset{1}{NO_2}.C_6H_4.\underset{4}{N}=N.C_8H_8.\underset{4}{N}=N.C_6H_4.\underset{1}{HO}.$$

This substance was obtained in the form of an orange powder,

slightly soluble in boiling alcohol and toluene, and readily soluble in hot aniline. All its solutions are orange-coloured; the addition of NaHO to the alcoholic solution changes the colour from orange to reddish-violet. The substance dissolves in sulphuric acid with a fine blue colour.

Paranitrobenzene-azometaxylene-azoresorcinol,

$$\underset{1}{NO_2}.C_6H_4.\underset{4}{N}=N.C_8H_8.\underset{4}{N}=N.C_6H_3.\underset{3}{HO}.\underset{1}{HO},$$

was obtained as a dark brown amorphous substance, dissolving with some difficulty in boiling alcohol, toluene, and glacial acetic acid, the solutions being of an orange colour. A specimen purified by deposition from hot toluene had a melting point of 231°. The substance dissolves in alcoholic soda with a fine red colour, which becomes violet on adding excess of alkali. It dissolves also with red colour in alcoholic ammonia and with blue colour in strong sulphuric acid. The alkaline solution poured into an acid-bath enables wool and silk to be dyed of a rich brown very similar to that imparted by triamidoazobenzene.

Secondary nitroazo-compounds analogous to the foregoing could not be obtained from the α-naphthylamine compound

$$C_6H_4<\begin{matrix}NO_2\\N_2.C_{10}H_6.NH_2\alpha'\end{matrix}$$

as the amido-group does not appear to be diazotised by the action of nitrous acid. By acting with $NaNO_2$ and an acid upon the corresponding β-naphthylamine compound a body having all the characters of a nitroso-derivative was obtained. This substance, which crystallises from alcohol in bright orange scales, and dissolves in acoholic potash with a violet colour, is undergoing further investigation.

Tertiary Azo-compounds.

$$Ph—N=N—R—N=N—R—N=N—Ph.$$

For reasons already explained, the secondary nitroazo-compounds could not be made available for the preparation of tertiary azo-bodies, but the diamidoazo-compounds previously described lent themselves readily to this reaction.*

* The constitutional formulæ here assigned to the new tertiary azo-compounds may safely be ascribed to the chief products of the action of the diazotised diamidoazo-bases upon alkaline solutions of phenols. The production of isomerides, as observed by Wallach in the preparation of his diazo-compounds, and by myself in the present case, considerably complicates the question of the relative positions of the substituents in these extremely complex bodies. The problem of the constitu-

β-Naphtholparaazobenzene-azo-α-naphthalene-azo-β-naphthol,

$$C_6H_4<\begin{matrix}\overset{1}{N}=\overset{\alpha}{N}-C_{10}H_6.\overset{\beta}{H}O\\ \underset{4}{N}=\underset{\alpha}{N}-C_{10}H_6.\underset{\alpha}{N}=\underset{\alpha}{N}-C_{10}H_6.\underset{\beta}{H}O.\end{matrix}$$

The diamidoazo-base, $C_6H_4<\begin{matrix}NH_2\\ N_2.C_{10}H_6.NH_2\alpha\end{matrix}$, was dissolved in dilute hydrochloric acid, and the theoretical quantity of sodium nitrite (2 mols.) gradually added to the well-cooled solution. The diazotising of the amido-groups is indicated by the change of colour of the solution from red to orange. On mixing this orange solution with an aqueous alkaline solution of β-naphthol a dull metallic green powder was precipitated, and this, after being collected and washed, was crystallised from boiling aniline. By this treatment the substance was separated into two distinct bodies, one of which (insoluble modification) crystallised out in small needles with a metallic green reflection, whilst the other remained in the aniline filtrate (soluble modification).

The crystalline portion dissolves in aniline with a violet colour; it is practically insoluble in boiling alcohol, acetone, or glacial acetic acid, and but very slightly soluble in chloroform and the benzene hydrocarbons. Boiling nitrobenzene dissolves the substance, giving a solution which is reddish-violet when hot, and blue-violet when cold. The melting point is above 295°.

The soluble modification was separated by diluting the filtrate with alcohol and neutralising the aniline with hydrochloric acid. A bulky violet precipitate was obtained, which after being collected and washed was purified by dissolving in alcoholic potash and filtering into water acidulated with HCl. This modification is more soluble in all solvents than the crystalline portion. It could not be obtained in a crystalline form.

The following results were obtained on analysis:—

Insoluble Modification.

I. 0·1794 gram gave 0·4950 gram CO_2, and 0·0762 gram H_2O.

II. 0·1666 gram gave 21·3 c.c. N at 18°, and 767 mm. bar. = 0·0248 gram N.

tion of the subsidiary isomeric products can of course be attacked with the greatest hope of success in the case of bodies of simpler constitution than those here dealt with. I may add that I have in the course of my experiments obtained results which seem to indicate that the production of the isomeride is to some extent governed by the conditions of the experiment, *i.e.*, the nature of the alkali and the solvent employed.

Soluble Modification.

I. 0·2907 gram gave 0·8025 gram CO_2, and 0·1216 gram H_2O.

II. 0·2902 gram gave 37·3 c.c. N at 19°, and 761·5 mm. bar. = 0 0429 gram N.

	Theory for $C_{36}H_{24}N_6O_2$.	Found. Insol. modification. I.	Found. Insol. modification. II.	Found. Sol. modification. I.	Found. Sol. modification. II.
C	75·52	75·25	—	75·29	—
H	4·19	4·71	—	4·64	—
N	14·68	—	14·88	—	14·78

These numbers show that the two bodies are isomeric, a result which has already been observed by Wallach in the preparation of disazo-compounds. The more striking characters of the two isomerides with respect to their behaviour towards solvents are set forth in the following table:—

Reagent.	Insoluble modification.	Soluble modification.
Glacial acetic acid..	Insoluble	Soluble at boiling point of acid. Solution violet when hot, blue when cold.
Alcoholic potash ..	Very difficultly soluble. Solution blue.	Readily soluble with a violet colour.
Strong H_2SO_4.....	A deep inky blue, becoming bluish-green and finally violet on dilution.	A clear indigo-blue, becoming brighter on dilution, and finally changing to violet.

A disulphonic acid corresponding to the foregoing compound, viz.:—

$$C_6H_4<\begin{matrix}\overset{1}{N}=\overset{\alpha}{N}-C_{10}H_5.\overset{\beta}{H}SO_3.\overset{\beta}{H}O\\ \underset{4}{N}=\underset{\alpha}{N}-C_{10}H_6.\underset{\alpha}{N}=\underset{\alpha}{N}-C_{10}H_5.\underset{\beta}{H}SO_3.\underset{\beta}{H}O,\end{matrix}$$

was obtained by mixing a solution of the diazotised diamidoazo-compound with an alkaline solution of β-naphtholsulphonic acid (Schäffer's). The salt (ammonium) of the acid is precipitated as a violet semi-gelatinous substance soluble in boiling water. Mineral acids precipitate the free disulphonic acid which is insoluble in boiling water. The acid possesses no tinctorial power.

The corresponding α-naphthol compound,

$$C_6H_4<\begin{matrix}\overset{1}{N}=\overset{\alpha}{N}-C_{10}H_6.\overset{\alpha}{H}O\\ \underset{4}{N}=\underset{\alpha}{N}-C_{10}H_6.\underset{\alpha}{N}=\underset{\alpha}{N}-C_{10}H_6.\underset{\alpha}{H}O,\end{matrix}$$

is very similar to the β-naphthol body. It forms a bronzy powder dissolving in alcoholic potash with a blue colour. The aniline solution is red, and it dissolves in strong sulphuric acid with an indigo-blue.

The phenol compound, of which the formula is most probably

$$C_6H_4<\begin{array}{l}\overset{1}{N}=\overset{4}{N}-C_6H_4.\overset{1}{H}O\\ \underset{4}{N}=\underset{\alpha}{N}-C_{10}H_6.\underset{\alpha}{N}=\underset{4}{N}-C_6H_4.\underset{1}{H}O,\end{array}$$

was obtained as a dull bronzy-green powder dissolving in boiling alcohol and toluene with an orange colour. The solution in alcoholic potash is violet, and the sulphuric acid solution dark indigo-blue.

The resorcinol compound was precipitated as a brown flocculent substance drying to a bronzy powder. The probable formula is

$$C_6H_4<\begin{array}{l}\overset{1}{N}=\overset{4}{N}-C_6H_3.\overset{3}{H}O.\overset{1}{H}O\\ \underset{4}{N}=\underset{\alpha}{N}-C_{10}H_6.\underset{\alpha}{N}=\underset{4}{N}-C_6H_3.\underset{3}{H}O.\underset{1}{H}O.\end{array}$$

This substance dissolves in alcohol with a dull red colour, and in alcoholic potash with a violet colour. The colour of the strong sulphuric acid solution is bluish-green.

With the exception of the β-naphthol compound none of the foregoing tertiary azo-compounds were readily crystallisable, and were not therefore examined in such detail.

β-Naphtholparaazobenzene-azometaxylene-azo-β-naphthol,

$$C_6H_4<\begin{array}{l}\overset{1}{N}=\overset{\alpha}{N}-C_{10}H_6\overset{\beta}{H}O\\ \underset{4}{N}=N-C_8H_8.\underset{\alpha}{N}=N-C_{10}H_6.\underset{\beta}{H}O.\end{array}$$

The diamidoazo-base was diazotised as before, and the orange-coloured solution gradually stirred into a solution of β-naphthol (2 mols.) in caustic soda. A deep violet precipitate was thrown down, and this, after being collected and washed, dried to a dull metallic-looking powder. The latter was dissolved in boiling aniline; the solution on cooling deposited small needles of a dull bronzy-green. The aniline filtrate was examined for an isomeride by dilution with alcohol and neutralisation with HCl and water, but only a very small quantity of a brown substance was thus obtained, and it was not possible to decide by analysis whether this was an isomeride or simply a trace of some bye-product.

A specimen of the crystalline substance was purified for analysis by dissolving it in boiling xylene. When cold the small green needles were collected and washed with pure benzene.

I. 0·1532 gram gave 0·4146 gram CO_2, and 0·0652 gram H_2O.
II. 0·1109 gram gave 14·4 c.c. N at 20·6°, and 768 mm. bar. = 0·0166 gram N.

	Theory for $C_{34}H_{26}N_6O_2$.	Found. I.	Found. II.
C	74·18	73·81	—
H	4·73	4·73	—
N	15·27	—	14·96

The substance dissolves in aniline with a reddish-violet colour, which becomes bluer on cooling. Its xylene-solution is also violet. It is practically insoluble in alcohol and glacial acetic acid, but dissolves in hot alcoholic potash with a bluish-violet colour. With concentrated sulphuric acid it gives a dull greenish-blue, becoming bright blue on dilution, and finally violet, and precipitating. It is transformed by the action of fuming sulphuric acid into a sulphonic acid which dyes silk and wool of a dull violet colour.

Action of Diazotised Paranitraniline upon Secondary Monamines.

Action upon Diphenylamine.

The starting point of this series of compounds was the body already described by Roussin and Poirrier (*Dingl. polyt. J.*, 1879, p. 423; *Chem. Industrie*, 1879, **2**, p. 293), obtained by the action of diazoparanitrobenzene upon diphenylamine.

On mixing an aqueous solution containing one molecule of diazotised paranitraniline with an alcoholic solution of diphenylamine (one molecule), a deep reddish-violet colour is produced, and the mixture soon becomes semi-solid from the separation of a dense brown precipitate. The latter was collected, washed with water, and basified by ammonium carbonate. A dull red substance was obtained which after crystallisation from dilute alcohol, formed brown leaflets having a melting point of 151°.

Paranitrobenzene-azodiphenylamine, $C_6H_4<\overset{NO_2}{N=N.C_6H_4.NH.C_6H_5}$, is readily soluble in alcohol with an orange colour, which changes to violet on the addition of hydrochloric acid, and the hydrochloride separates out in clusters of small needles having a beautiful violet reflection. The salt is extremely unstable, being instantly decomposed by water or by exposure to the air. The base dissolves in strong sulphuric acid with a violet colour.

Paraamidobenzene-azodiphenylamine, $C_6H_4<\overset{NH_2}{N=N.C_6H_4.NH.C_6H_5}$.—

The reduction of the nitro-base was effected by adding ammonium sulphide to the cold alcoholic solution. In the course of a few minutes the colour of the solution changed from orange to yellow, and on diluting with water an orange crystalline substance slowly separated out. The amido-base thus obtained was mixed with a small quantity of some secondary product containing sulphur, from which it could not be entirely freed even by repeated solution in dilute HCl, filtration, and reprecipitation by ammonia. It was found, however, that this impurity was removed by the diazotising process, so that no further attempts at purification were made, and the following remarks apply to the crude substance.

The melting point of the crude base is 90—91° C. Its salts dissolve readily in water with a magenta colour. The base itself is but slightly soluble in boiling water, but dissolves readily in alcohol, acetone, chloroform, and the benzene hydrocarbons with a yellow colour. On adding hydrochloric acid to the alcoholic solution, a green colour is first produced, and this on the further addition of acid passes into red. The solution in concentrated sulphuric acid is violet passing into red on dilution. The salts act as dye-stuffs, imparting a bright yellowish-orange shade to silk and wool.

β-Naphtholparaazobenzene-azodiphenylamine,

$$C_6H_4\begin{cases}{}^{1}N{=}{}^{\alpha}N{-}C_{10}H_6.{}^{\beta}HO \\ {}^{4}N{=}{}^{4}N{-}C_6H_4.\underbrace{NH.C_6H_5}_{1}\end{cases}.$$

In order to diazotise the amido-base, $C_6H_4\begin{cases}NH_2 \\ N_2\end{cases}C_6H_4.N<\begin{matrix}H \\ C_6H_5\end{matrix}$, it was found most advantageous to dissolve it in alcohol with the addition of hydrochloric acid, and then add the theoretical quantity of $NaNO_2$ dissolved in water little by little to the well cooled solution. The orange-coloured solution was then gradually mixed with an aqueous solution of sodium β-naphtholate. A reddish precipitate was obtained which was collected, washed and dried. Purification was effected by dissolving the substance in alcoholic soda, filtering, and precipitating by an acid. This operation was repeated several times, and finally a violet precipitate was obtained which, after being collected and washed with water till free from saline impurity, dried to a dull bronzy powder. After crystallisation from hot glacial acetic acid it was obtained in the form of warty scales having a dull bronzy lustre and melting at 203—204° C.

I. 0·3301 gram gave 0·9128 gram CO_2, and 0·1471 gram H_2O.
II. 0·1558 gram gave 21·2 c.c. N at 22° and 767·1 mm. bar = 0·0242 gram N.

	Theory for $C_{28}H_{21}N_5O$.	Found. I.	Found. II.
C	75·84	75·41	—
H	4·74	4·98	—
N	15·80	—	15·53

This new secondary azo-compound is characterised by the following properties:—It dissolves slightly in boiling alcohol and readily in benzene with a red colour. It is dissolved by glacial acetic acid, the solution being red when hot, and reddish-violet when cold. It dissolves in strong sulphuric acid with a greenish-blue colour, changing to reddish-blue on standing. Alcoholic potash or soda dissolves the substance with great facility, the solution being red. A most characteristic property of this compound is the fine blue coloration produced by adding hydrochloric acid to its dilute solution in alcoholic potash.

These researches have been conducted in the course of technological studies carried on in the laboratory of Messrs. Brooke, Simpson, and Spiller at the Atlas Works, Hackney Wick; and it is with great pleasure that I record my thanks to this firm. The investigations will be extended to the action of diazoparanitrobenzene upon tertiary monamines and phenols, and the corresponding series of reactions with the isomeric nitranilines and their homologues.

LXI.—*On the Production of Hydroxylamine from Nitric Acid.*

By Edward Divers, M.D., Principal of the Imperial Japanese College of Engineering.

During the last few months I have resumed an investigation of the conversion of free nitric acid into hydroxylamine, which I began in 1872, but the pursuit of which I had soon after to relinquish. So far as I can learn, this field of research has in the interim not been occupied, and I am therefore in a position, with the aid of recent work, to publish something of interest on this subject as yet unrecorded.

Lossen having discovered hydroxylamine in 1865 by reducing ethyl nitrate with tin and hydrochloric acid, Maumené followed by showing that for ethyl nitrate ammonium nitrate might be substituted (*Compt. rend.*, 1870). Having confirmed for my own satisfaction the accuracy of Maumené's observations, I found that sodium nitrate could be equally well employed, and then, proceeding one step further, that nitric acid itself could be used with excellent results. My further work, then and since, forms the subject of this communication.*

Experiments with Tin.

Tin is I believe the only metal which has hitherto been known to produce hydroxylamine, and then only in conjunction with hydrochloric acid. This metal will, however, not only convert nitrates and nitric acid into hydroxylamine when used with hydrochloric acid, but will also form this base by acting alone upon pure dilute nitric acid. In attempting to verify this statement, it will be found very easy to fail. A 3 or 4 per cent. solution of nitric acid, free from other acids (or a false appearance of success will be almost certain), should be left on an abundance of granulated tin for about half an hour, after which

* In *Watts's Dictionary*, 1st Suppl., 1872, full mention is made that nitric acid yields hydroxylamine when treated with tin and hydrochloric acid, but no authority is given for the statement. Groves, in the account he gives of hydroxylaminæ in the last edition of *Miller's Chemistry*, 1878, makes no mention of the reduction of nitric acid itself. The same is true of Roscoe and Schorlemmer in their *Treatise on Chemistry*, 1878; Acworth and Armstrong in their elaborate paper "On the Reduction of Nitric Acid" (Part I), in this Journal for 1877, recognise the possibility of hydroxylamine being a source of the nitrous oxide produced by nitric acid acting on metals, but do not treat of its formation in this way as an ascertained fact.

So little indeed does this fact of the formation of hydroxylamine by the action of metals upon nitric acid appear to be known, that in all the discussions of the difficulties in estimating nitrates and nitrites as ammonia produced in acid solutions

hydroxylamine may generally be detected in the usual way.* Nitric acid, after standing a sufficient time upon tin, no longer yields hydroxylamine. Ammonia is one of the products in all cases, whether the nitric acid is dilute or the strongest that will act upon tin, and at any stage of the action.

Tin and Sulphuric Acid.—In examining the effect of sulphuric acid upon the reaction between nitric acid and tin, two comparative experiments were carried on together. In each experiment about 45 grams of granulated tin were placed in a flask filled with carbon dioxide gas,† and a solution poured in, measuring 250 c.c., and containing in one case 5 grams of nitric acid (hydrogen nitrate) alone, in the other case the same quantity of nitric acid together with 20 c.c. of sulphuric acid, about $4\frac{1}{2}$ mols., that is, to 1 mol. of nitric acid. The flasks were closed and set aside for two days in very hot weather, there being scarcely any evolution of gas. Much grey and dense stannoso-stannic hydroxide was deposited, about the same quantity in each, and the solutions became yellow. But the solutions differed in composition. That without sulphuric acid contained some stannous salt dissolved and a very little stannic salt, but no hydroxylamine. The sulphuric acid solution contained much hydroxylamine, much stannous salt, and so much stannic salt as to give a copious precipitate with water. These tin solutions proved very unstable, but would no doubt have been much less so in winter, when there would also have been formed much less stannic salt; but these points are here unimportant, except perhaps to those who may repeat the experiments. These parallel experiments demonstrate the great effect of sulphuric acid upon the yield, if not upon the production, of hydroxylamine.

Another experiment was made, in which the sulphuric acid and nitric acid were diluted scarcely more than sufficient to allow of their free action upon the tin; for without some dilution there is hardly any action. In this experiment 5 grams (1 mol.) of nitric acid and 35 grams ($4\frac{1}{2}$ mols.) of sulphuric acid, diluted to about 62 c.c. only of solution, were poured upon 35 grams of tin contained in a flask filled with carbon dioxide, and having its mouth loosely stopped. Action was at once apparent by the heating up of the mixture and the escape of nitrogen oxides, but it never grew violent, and the amount of gases evolved was not very great. Nitric oxide constituted the bulk of

—even as late as that contained in a paper in the *Chem. News*, **46**, 63, by Kinnear—no reference is made to it.

* Namely, by treating the liquid with hydrogen sulphide and filtering off the tin sulphide, adding copper sulphate in the least possible excess and filtering off the copper sulphide, and lastly, adding potassium hydroxide in excess to precipitate cuprous oxide by means of the hydroxylamine.

† To exclude air.

these gases, but at first red vapours were set free, and afterwards nitrous oxide. Effervescence soon ceased, and then the solution was clear and colourless. At first it had been milky white, but probably only from very fine effervescence. The tendency to heat up soon ceased to show itself, and altogether the action was strikingly moderate, considering that about 11 grams of tin (a little more than 1 atom) went into solution. The liquid poured off and diluted to 1 litre gave a copious cream-yellow precipitate of stannoso-stannic hydroxide, which rapidly bleached by oxidation on exposure to the air. The mother-liquor contained sulphuric acid and ammonia, but neither nitric acid, hydroxylamine, nor tin salt. The effect, therefore, of scarcity of water is to cause higher oxidation of the tin, and this apparently at the expense of the hydroxylamine, which changes to ammonia. Von Dumreicher (this Journal, Abstr., 1882) has pointed out the readiness with which stannous salts and hydroxylamine react: $NH_3O + SnO = NH_3 + SnO_2$.

Tin and hydrochloric acid, as stated in *Watts's Dictionary*, 1st Suppl., convert nitric acid into hydroxylamine. Hydrochloric acid exerts a still more striking influence upon the production of hydroxylamine by tin than sulphuric acid. While with nitric acid alone only traces of hydroxylamine can be obtained at all, and even these only by watchful precautions, this substance is obtained in abundance in presence of hydrochloric acid under almost any circumstances. Although I have made many experiments upon the production of hydroxylamine in this way, there are only two which need be recorded here. One of these illustrates a reaction which appeared to me, when I first observed it years ago, as little less than marvellous. This is the reaction of concentrated nitric and hydrochloric acids (*aqua regia*) with granulated tin. Taking about 8 mols. of hydrochloric acid in fuming solution to 1 mol. of nitric acid sp. gr. 1·42, and pouring the mixture upon tin, very little gas if any is evolved, nearly all the nitric acid is converted into hydroxylamine, the tin is dissolved as stannous chloride, and the action, though energetic, is quite under control and very soon completed. If the acids are mixed some time before use, and in hot weather, the evolution of chlorous gases renders the storage of the mixture in bottles almost unmanageable. It is better, therefore, to mix the acids just before using them, although tin will at once bleach the orange mixture on coming in contact with it, and but little hydroxylamine will be destroyed. An experiment illustrative of this action I shall now describe. Fuming hydrochloric acid, 58 c.c., and nitric acid, 1·42 sp. gr., 5 c.c., that is, about 9 mols. of hydrochloric acid to 1 of nitric acid, were mixed, and quickly poured upon 35 grams of granulated tin lying in a flask filled with carbon dioxide. The flask, loosely corked, was plunged into a pail of water and agitated.

At first boiling occurred, but the vapours evolved appeared to be only hydrochloric acid and water. This soon ceased, and soon after, the development of heat also. The solution was poured off, and the tin found to have diminished in weight 21 grams, or about $2\frac{1}{4}$ atoms. Of the solution, diluted with the washings of the tin to 500 c.c., 25 c.c. were measured off, further diluted, deprived of tin by hydrogen sulphide, and of the latter by carbon dioxide gas, and then treated with decinormal solution of iodine, with addition of sodium carbonate to keep the solution alkaline. The 25 c.c. required 69 c.c. of iodine solution, and therefore, reckoning 2 atoms of iodine as indicating 1 mol. of hydroxylamine, the quantity of nitric acid converted into this substance was $4\frac{1}{3}$ grams out of 5, and the quantity of hydroxylamine itself $2\frac{1}{4}$ grams. It thus appears that, carried out in this way, the reduction of nitric acid by tin and hydrochloric acid is well suited for preparing hydroxylamine.*

The other experiment I record is one differing from the last in the acids being diluted to 250 c.c., and left on the tin for two days. No gas was given off, and about 21 grams ($2\frac{1}{4}$ atoms) of tin were dissolved. In this case a little more than half the nitric acid was found as hydroxylamine.

Von Dumreicher has shown (*loc. cit.*) that stannous chloride in acid solution reduces nitric acid to hydroxylamine, and this again to ammonia. He states, however, that the conversion of the hydroxylamine into ammonia proceeds nearly at the same rate as its formation, and that consequently the reaction of nitric acid and stannous chloride is not available for the preparation of hydroxylamine. So that from his observations it follows that the formation I have here described of this base is the result of the primary reaction of the tin and acids, and is independent of the operation of stannous chloride, and that on the other hand the formation of ammonia is largely owing to the action of this salt. It is probable, too, that the smaller yield of hydroxylamine when sulphuric acid is used instead of hydrochloric acid, is to be attributed to a greater deoxidising action by stannous sulphate than by stannous chloride.

* The precipitation of the tin as sulphide, and the evaporation of so much acid are very troublesome operations, and the latter is destructive. Victor Meyer has lately (*Ber.*, 1882, 2) brought to notice again the use of sodium carbonate to precipitate the tin and neutralise the acid, a process described ten years ago in *Watts's Dictionary*, 1st Suppl. (p. 723). Another method which probably works well is that recommended by Bertoni (this Journal, Abstr., 1880) of removing tin and hydrochloric acid by litharge. I may shortly be able to offer to the Society an account of the actual preparation of hydroxylamine from nitric acid by tin.

Experiments with Zinc.

Zinc is very effective in converting nitric acid into hydroxylamine. Ammonia is always produced at the same time. In the presence of another acid hydroxylamine is easily obtained, but traces of it can also be obtained from nitric acid alone. If nitric acid of the dilution recommended for the similar experiment with tin is poured upon granulated zinc and very shortly poured off again, hydroxylamine may generally be detected by Lossen's copper test. To guard against deceptive appearance of success, care must be taken, as with tin, to use nitric acid free from either hydrochloric acid or sulphuric acid. Failure in this experiment is not unfrequent, but the trouble of repeating the experiment is much less than in the case of tin, inasmuch as the dissolved zinc, unlike the tin, need not be removed before applying Lossen's test.

Zinc and Sulphuric Acid on Hydrochloric Acid.—The production of hydroxylamine from nitric acid by the action of zinc and sulphuric acid takes place so readily, and the presence of hydroxylamine is in this case so easy to demonstrate, that it furnishes a good experiment for the lecture-room, which may be thus performed:—Pour some dilute sulphuric acid on zinc and then a little nitric acid, when the effervescence will lessen to a marked extent; in half a minute pour off the acid solution and add potassium hydroxide in large excess to dissolve zinc hydroxide, and then a very little copper sulphate solution, when a copious yellow precipitate will be obtained on stirring.

I have made a number of quantitative experiments to determine the extent of the formation and destruction of hydroxylamine by nitric acid, and either sulphuric or hydrochloric acid acting upon zinc. These are not complete as a series, but serve to demonstrate several points. The hydroxylamine was estimated by decinormal iodine solution according to the reaction $2NH_3O + 2I_2 = N_2O + H_2O + 4HI$ (Meyeringh). The hydroxylamine solution measured off was mixed with sodium carbonate solution until there remained suspended in it some zinc carbonate, a salt which has no action on iodine. Starch did not work well with the carbonate precipitate, and was therefore not used. But this caused no inconvenience, as the bleaching of the iodine solution was very evident in presence of the white precipitate. The zinc carbonate, however, neutralises the last portions of hydriodic acid but slowly, so that for an hour after the rough finish of the titration, small additions of iodine are required. Practice simplifies matters by teaching what excess of iodine may be added at first, while the end-reaction when reached is sharply enough defined. By keeping sodium carbonate slightly in excess (it becomes of course acid carbonate), the end-reaction can be reached at once; but there is

a risk of adding too much, and with a number of titrations on hand, the other method was deemed safer. The results are best expressed, I think, in terms of the nitric acid converted into hydroxylamine out of 100 parts taken. As nitric acid wholly converted to hydroxylamine would yield 52·38 per cent. of its weight, or roughly stated half its weight, half the percentages of nitric acid will express those of hydroxylamine.

A table of the results of these experiments is here inserted, which needs a little explanation, and the addition of some remarks to make it clear, and to enable me to simplify the statement of my conclusions

Percentage Amounts of Nitric Acid left as Hydroxylamine by the Action of Zinc and another Acid.

1. Hydrochloric Acid, without cooling.

	Equivalents of hydrochloric to one nitric acid.				
	3.	5.	7.	9.	11.
2 minutes	16·0	19·3	23·2	23·2	16·4
5 „	13·8	17·1	lost	12·6	5·7
10 „	13·1	14·6	15·1	8·7	3·5
3 hours	11·5	11·4	10·5	3·7	1·1

2. Hydrochloric Acid, with cooling.

	Equivalents of hydrochloric to one nitric acid.					
	3.	5.	7.	9.	(9).	11.
2 minutes	12·7	16·0	22·1	21·0	(27·9)	24·4
5 „	18·1	20·7	26·3	23·8	(32·5)	23·5
10 „	17·3	18·0	22·8	16·8	(27·9)	19·1
1½ hours	16·2	15·6	18·9	13·1	(17·4)	9·8

3. Sulphuric Acid, with cooling.

	Equivalents of sulphuric to one nitric acid.					
	3.	5.	7.	9.	(9).	11.
2 minutes	8·4	17·4	18·2	20·0	(13·7)	25·1
5 „	18·3	29·6	31·2	31·9	(29·0)	39·1
10 „	20·8	32·9	39·7	35·3	(35·1)	47·0
1½ hours	21·7	32·0	34·0	22·6	(21·3)	25·0

respecting the course of the reduction of nitric acid to hydroxylamine by zinc in presence of another acid, these conclusions being drawn from the results in this table and others allied to them.

Three series of experiments are tabulated, each of which was completed in one day, excepting the duplicate experiments, the results of which are placed in brackets. The quantity of liquid was in every case a quarter-litre, consisting of water holding five grams of hydrogen nitrate and 3, 5, 7, 9, or 11 equivalents of these five grams, of hydrochloric or sulphuric acid, as shown in the table. It will be seen that the acidity of the liquids varied greatly, being in the experiments recorded in the last column, three times that of the solutions used in the experiments of the first column. In the first series of experiments 70 grams of granulated zinc were taken in each case, but in the other series only 35 grams, in order to make the reduction slower. The experiments were made in hot summer weather; the first series without cooling, the others with cooling by shaking the flasks in well-water during the reaction. The very large surface of zinc exposed, and the want of cooling in the first series of experiments, led to the more acid liquids becoming boiling hot and continuing so for a few minutes. Effervescence occurred in all cases, but from being very mild and creamy where only three equivalents of the other acid were present, became violent and coarse—bubbled when nine and eleven equivalents of the acid were used. The effervescence ceased soonest where least acid was used; in the first series the time it stopped was about $2\frac{1}{2}$ minutes with 3 equivalents of acid, to 9 minutes with 11 equivalents; in the second series from $6\frac{1}{2}$ minutes with 3 to $9\frac{1}{2}$ with 11 equivalents; and in the third series from $8\frac{1}{2}$ minutes with 3 to 17 minutes with 11 equivalents, counting from the beginning of the experiments. In the first series cooling not being practised, the liquid grew turbid during the course of the experiment, much zinc hydroxide being deposited. This did not happen when only three equivalents of hydrochloric acid had been used until 15 minutes, long after effervescence had ceased. But, approaching regularly through the intermediate cases, the times of appearance of turbidity and of cessation of effervescence became identical in the last one where 11 equivalents of acid had been added, namely, at nine minutes from the commencement. Another noteworthy circumstance was, that though all the solutions were clear at the end of five minutes, portions of them then removed slowly became turbid on standing, and deposited a marked quantity of zinc hydroxide; that in the three-equivalent experiment most slowly; and that in the eleven-equivalent experiment most quickly, and in a very short time. In the second and third series of experiments—that is, those in which artificial cooling was applied—zinc hydroxide was not deposited even after considerable time.

The extent to which the nitric acid was decomposed requires to be noticed, as this was full in some only of the experiments. Where only three equivalents of sulphuric or hydrochloric acid were used, considerable quantities of nitrate remained after the acids had become neutralised by the zinc. With the use of more and more of the second acid, the quantity of nitrate left was found to be very markedly less and less, a trace only with nine equivalents of the second acid, and none at all with eleven in the case of cooling. After conversion to zinc salt, the nitrate is slowly reduced by the excess of zinc to nitrite, so that while after but five minutes' action nitrite is only to be found with doubt, it is abundant after one or two hours.*

Nitrite and hydroxylamine salt are thus found together in solution, although in acid solutions they at once destroy each other (V. Meyer). Where nitrate had almost or entirely disappeared by the action, no nitrite was detected. Ammonia was always found, whether the solutions were examined shortly after they had been in contact with zinc or at any later stage. Most ammonia was present where all the nitric acid had been reduced, and where the hydroxylamine from it had been most destroyed.

In testing for ammonia with potassium hydroxide, the precaution was taken of first destroying hydroxylamine with iodine. There was generally, however, no difficulty in directly detecting the ammonia with platinum chloride. The nitrite was detected by the ferrous sulphate reaction. In a number of cases its quantity was imperfectly estimated by the iodine method in the following way:—After determining the hydroxylamine by iodine, the liquid was acidulated, and this iodine again liberated by reaction between hydrogen iodide and hydrogen nitrite; then as quickly as possible this iodine was titrated with sulphurous acid. The quantities of nitrite being small and of hydrogen iodide large, the atmospheric action upon the latter was too rapid to leave the results very accurate.

Having now described summarily the experiments of which the principal results have been arranged in the table, I proceed to state some deductions from these and other experiments as to the influence of some of the circumstances upon the results.

First, as to the Relative Effect of the Two Acids.—The action of hydrochloric acid upon zinc is much more rapid than that of sulphuric acid. Hence hydrochloric acid becomes more rapidly neutralised, and out of the field of activity, as regards nitric acid and hydroxylamine, while its solution grows hotter, and therefore must make other changes go on more rapidly. Either indirectly from the greater activity of this acid upon zinc, or directly by some action upon nitric acid

* This change is in accordance with the known reducing action of zinc and other metals upon their nitrates in solution.

and hydroxylamine, greater than that of sulphuric acid, the increase in quantity of the hydroxylamine and the decrease which follows, occur more rapidly with hydrochloric acid. It is also difficult, if not impossible, with strong solutions at least, to get a yield of hydroxylamine with this acid as good as that with sulphuric acid.

Secondly, as to the Effect of the Proportion of the other Acid to the Nitric Acid.—The greater this is, the greater is the proportion of the nitric acid which can be found converted to hydroxylamine. The experiments I have tabulated, in which sulphuric acid was used, are in agreement with this proposition, but those in which the acid was hydrochloric show rather a maximum of hydroxylamine from the same weight of nitric acid, when but seven to nine equivalents of hydrochloric acid were present. I have, however, the results of other experiments relating to this point, which are more positive, while those here given were certainly affected by another circumstance leading to the destruction of the hydroxylamine. The evidence afforded of this being the case, by the duplicate experiments with nine equivalents of hydrochloric acid, is alone almost sufficient on this point, for we see from these that there may be a much greater difference between two similar experiments, both with nine equivalents of acid, than between two in which nine and eleven are used. Now, these experiments were all performed, to the best of my ability and knowledge, in the same way in everything. The one circumstance liable to vary, and easily escaping regular control, was the rise in temperature, in consequence of its highly cumulative rate. Hydrochloric acid solutions, so strong as were those used in the nine and eleven equivalent experiments, are thus too active for their purpose, and are so destructive to hydroxylamine in contact with zinc as to mask the effect of varying degree of acidity. It will be seen that, owing to this, the descent in equal times from the maximum quantity of hydroxylamine is much more marked with the use of the larger than with the smaller quantities of acids.

The other experiments to which I have referred in this connection were so carried out for me, that on equal weights of granulated zinc were poured equal volumes of acid mixtures having equal degrees of total acidity. The solutions were poured off the zinc when the fulness of the effervescence was over, and then titrated for hydroxylamine. The series was carried as far as 35 equivalents of hydrochloric acid, and still more of sulphuric, to one of nitric acid; and the proportion of nitric acid found converted to hydroxylamine became greater and greater with the increase in the proportion of the second acid, until so much as 80 per cent. of the nitric acid was thus obtained. The acid liquors were in these experiments very weak, and also, as already mentioned, of the same acidity; rise in temperature, therefore, and its

variations, did not appreciably affect the results. But this series of experiments is open, I fear, to the objection that where such large quantities of the second acid were used, the nitric acid was too little to render the estimation of the hydroxylamine quite reliable.

Thirdly, as to the Effect of the Proportion of Water Present.— Strong sulphuric acid mixed with a little nitric acid has no sensible action upon zinc. Slightly diluted acid is active in proportion to the water present, but as heat is generated, cooling is required to keep the action steady. When the concentration is such that 1 gram of sulphuric acid is contained, along with nitric acid, in not more than $2\frac{3}{5}$ c.c. of solution, the zinc is freely attacked without escape of hydrogen, but if the dilution is greater, hydrogen escapes. At first a very moderate effervescence goes on, the escaping gas being principally nitrous oxide, if the nitric acid is present in a proportion of not more than 1 mol. to $3\frac{1}{2}$ of sulphuric acid (1 gram to 5·44 grams). By working in this way upon 5 grams of nitric acid with sulphuric acid in the proportion of $3\frac{1}{2}$ mols. to 1, keeping the mixture cool while actively agitating for about 40 minutes, nearly the calculated number of grams ($15\frac{1}{2}$) of zinc dissolved and yielded much hydroxylamine. The time in which a given weight of zinc dissolved, necessarily varied with the amount of surface exposed and other circumstances, but the weight dissolved corresponded approximately (in my very few experiments) to the nitric acid decomposed, and to the hydroxylamine obtained. The quantity of nitric acid thus obtained as hydroxylamine was about 0·36 of the whole. In another experiment, where the sulphuric acid was somewhat more concentrated, and in the proportion of $4\frac{1}{2}$ mols. to 1 of nitric acid, water was gradually added in small quantity until effervescence of hydrogen became evident, and the amount of hydroxylamine found was almost the same. But in another experiment again, where also $4\frac{1}{2}$ mols. of sulphuric acid were used, and where the dilution was from the first the same as that existing only in the latter part of the preceding experiment, the hydroxylamine was only half as much, although $15\frac{1}{2}$ grams of zinc had here also dissolved. Hydrogen and nitrous oxide escaped all through the reaction in this case.

When the quantity of water in the case of the use of hydrochloric acid is so small that *aqua regia* is abundantly formed, the action of the two acids upon zinc is very violent, and the temperature cannot be kept down. A little hydroxylamine remains at the end of the reaction, but that probably is what has formed in the last period of it. With greater dilution, abundance of hydroxylamine is obtained by the use of either sulphuric or hydrochloric acid, and I conclude from the results of much, but irregular experimentation, that, beyond the least quantity sufficient for chemical action to proceed freely, additional

water acts only indirectly—moderating the rise in temperature and lowering the rate of progress of the reactions, and so rendering it easier to control them, and at the time of the best yield of hydroxylamine to separate the solution from the undissolved zinc. But further testing of this conclusion is needed to confirm it.

Fourth, as to the Effect of Rise of Temperature.—Rise in temperature quickens, as was to be expected, both the formation and destruction of hydroxylamine by zinc. This is very apparent on comparing the first and second series of experiments. Its destruction seems to be accelerated in this way, much more than its formation, but this is a matter also requiring further experiments. Rise in temperature causes the formation of basic solutions, which deposit zinc hydroxide, as may be learned from my description of the tabulated results of experiments. A close connection almost certainly exists between this effect and the destruction of the hydroxylamine, as will be explained when considering the nature of the process of conversion of the hydroxylamine into ammonia.

Experiments with other Metals.

Magnesium.—From its relations to zinc, magnesium ought to form hydroxylamine from nitric acid, and on trial it has been found to do so. But the hydroxylamine is formed and decomposed again very rapidly, and is therefore very apt to escape detection. To obtain it, dilute hydrochloric acid appears to be necessary, sulphuric acid having always proved useless.

Cadmium, in the granulated state, produces small quantities of hydroxylamine from nitric acid in presence of either hydrochloric or sulphuric acid.

Lead.—It remains doubtful whether this metal can give hydroxylamine with nitric acid. Out of very many trials, in only one was a small quantity of hydroxylamine detected. Hydrochloric acid was used in all the trials, and ammonia was always formed. Lead dissolving in nitric acid alone also gives ammonia.

Aluminium.—A mixture of sulphuric and nitric acids is known to be without sensible action upon aluminium. A mixture of dilute hydrochloric and nitric acids may remain for some time on aluminium without hydroxylamine becoming present, but when the effervescence has nearly ceased, and if the whole has been immersed in cold water to keep off the violent accession of action which is apt otherwise to set in, decided though small quantities of hydroxylamine are usually to be found.

Iron always fails to yield hydroxylamine, though it produces much ammonia.*

* In the last *Dublin Pharmacopœia* there was a formula for the preparation of

Sodium, in form of amalgam, and not in such quantity as to neutralise the acid, has failed to give any hydroxylamine, but gives abundance of ammonia. By its action upon sodium nitrate or nitrite, it produces hyponitrite and hydroxylamine also.

Copper, *mercury*, *silver*, and *bismuth* all fail to produce either hydroxylamine or ammonia from nitric acid.

Other Experiments.

Stannous chloride reduces nitric acid to hydroxylamine and ammonia, as pointed out by von Dumreicher (*loc. cit.*). Stannous chloride solution dissolves nitric oxide, and it is probably the decomposition by hydrochloric acid of the compound thus formed, and not the union of *nascent* hydrogen with nitric oxide, as commonly represented, that gives hydroxylamine, when tin, hydrochloric acid, and nitric oxide are digested together. Copper nitrate, in the presence of copper and nitric acid—the equivalent that is of cuprous nitrate—exercises the reducing action from which nitrous oxide results when copper is treated with nitric acid. (Acworth and Armstrong.) Attempts to convert nitric oxide to hydroxylamine by dissolving it in ferrous sulphate and pouring the solution, mixed with sulphuric acid upon zinc, failed, as might have been anticipated, by the greater activity of ferrous salts than stannous salts in reducing hydroxylamine. *Ferrous hydroxide* reduces nitrates to ammonia, nitrous oxide, nitrogen, and, according to Zorm (*Ber.*, 1882, 1), hyponitrite.

Reduction of Nitrous Acid to Hydroxylamine.—Hydroxylamine is produced by reducing nitrites with sodium or potassium. It is difficult to obtain satisfactory evidence as to whether nitrous acid yields hydroxylamine or not, but there can be little hesitation in believing that it does. Sodium nitrite solution was prepared from some pure silver nitrite, and tried both with tin and hydrochloric acid and

solution of ferric nitrate, in which the quantity of nitric acid ordered was insufficient for the terms of the chemical equation: $2Fe + 8HNO_3 = Fe_2(NO_3)_6 + 2NO + 4H_2O$. When this pharmaceutic formula was transferred to the first edition of the *British Pharmacopœia* (1864), it received some severe criticism, as being a process that could not yield a normal nitrate, and that gave, as was accordingly to be expected, a basic unstable solution. In the new edition of the *Pharmacopœia* (1867) the formula was so altered as to raise the proportion of nitric acid to the quantity required by the above theory. Now, as a matter of fact, the old formula gave a beautifully bright-coloured solution, and quite stable, which is saying much for nitrate of iron solution, while the present one gives an acid preparation, the explanation being that though the gas given off is indeed nearly pure nitric oxide, much of the nitric acid becomes ammonium nitrate during the dissolution of the iron, and this is a product more deoxidised than nitric oxide. Less nitric acid therefore is required than is indicated by the above equation.

with zinc and hydrochloric acid. Sometimes success was attained with zinc, the successful way being to drench some granulated zinc with weak sodium nitrite solution, and then pour on dilute hydrochloric acid. It will be seen that such experiments are open to the objection that the nitrous acid, on being set free in any quantity, will decompose into nitric acid, nitric oxide, and water, and that then the nitric acid, or even the nitric oxide, may furnish the hydroxylamine. In the successful experiments no nitrous smell or colour was however observed. According to von Dumreicher, sodium nitrite gives pure nitrous oxide with acid stannous chloride.

On the Nature of the Reduction of Nitric Acid.

In their relation to nitric acid metals must be divided into two classes, exclusive of the inactive metals, one formed of those which produce ammonia from it, and the other of those which do not. To the former belong tin, lead, zinc, cadmium, magnesium, iron, aluminium, potassium, sodium, and others; while the latter includes copper, mercury, silver, bismuth, and others. Metals of the latter class leave all the hydrogen of the nitric acid combined with oxygen as water.

With this fact before us, there seems to be but one way of interpreting the action of the silver-class of metals upon nitric acid, and that is to recognise that these metals combine with the nitrogen of the acid, and do not decompose its hydroxyl. This combination with nitrogen rather than oxygen is already known to take place in other cases, even in presence of water, as when ammonia and the oxides of these metals are brought in contact. In accordance with current notions of molecular interchange, this action of these metals on nitric acid is represented by the following equations:—

$$2Ag + HONO_2 = HOAg + AgNO_2,$$
$$HOAg + HONO_2 = AgONO_2 + H_2O,$$
$$\text{and } AgNO_2 + HONO_2 = AgONO_2 + HNO_2,$$

of which only the first needs consideration here. The interest of this equation lies in its representing the nitrogen as undergoing no change in quantivalence, and the metal as combining directly with the nitrogen, and thus making out silver nitrite and nitrites to be *nitronates*. The conversion of other nitrites to the silver salt by double decomposition is greatly in favour of viewing them as having all the nitronate constitution. The nitronate structure seems also to furnish a definite reason for the loss of oxygen by potassium nitrate when heated, in the metallic radical parting from oxygen to unite directly with the nitrogen, thus:—

$$2KONO_2 = 2KNO_2 + O_2.*$$

On the other hand it is hardly to be doubted that the nitrous ethers are true nitrites, the nitro-paraffins being nitronates.

As regards the formation of a basic substance, silver hydroxide, as represented in the equation, it will be seen that this is in agreement with the known action of metals of the other class upon metallic nitrates, for example—

$$2Na + NaONO_2 = NaONa + NaNO_2$$
$$Zn + Zn(ONO_2)_2 = ZnO_2Zn + Zn(NO_2)_2$$
$$\text{and } 2Pb + 2NaONO_2 = (NaO)_2Pb + Pb(NO_2)_2.$$

Having treated of the action of the silver class of metals upon nitric acid as including the union of the metal directly with the nitrogen, in accordance with what appears to be the requirement of the facts, I may now notice the difficulties in accepting the view that the metal unites directly only with oxygen. Recognising that the metal does not replace hydrogen, the symbolic expressions become—

$$2Ag + HONO_2 = HONO + Ag_2O$$
$$\text{and } Ag_2O + 2HONO_2 = 2AgONO_2 + H_2O.$$

* Is there not in the nitronic constitution of nitrous acid a likely explanation of the advantage of *red nitric acid* in dissolving metals of the silver class, that one atom of the metal displacing the hydrogen of the nitronic acid, another can at the same moment more readily displace the hydroxyl of the nitric acid when assisted by the hydrogen from the nitronic acid?—

$$2Ag + HNO_2 + HONO_2 = 2AgNO_2 + H_2O.$$

Have we not also in this constitution an easy conception of the nature of the formation of nitrogen tetroxide from nitric acid and nitronic acid—

$$HNO_2 + HONO_2 = H_2O + (NO_2)_2,$$

and of the reverse action of nitrogen tetroxide on potassium hydroxide to form nitrite and nitrate?

Note by Dr. Armstrong.—The action of *red nitric acid* is sufficiently explained by the presence in it of nitrous acid, or it may be of a compound of nitrous and nitric acids. Russell's experiments leave practically no doubt that nitric acid is without action on silver. In like manner, platinum is not attacked by nitric acid, but will dissolve if alloyed with silver; no doubt, because nitrous acid is produced by the dissolution of the silver. Why nitrous acid is a solvent of silver and platinum, while nitric acid is not, we do not exactly know, although probably in the case of the latter metal, the formation of a *platonitrite* plays an important part.

With reference to the formation of N_2O_4 during the dissolution of metals, &c., in nitric acid, I some time ago satisfied myself by experiment that it is produced by the reaction here formulated by Dr. Divers, and there is, I believe, no doubt that whatever the nature of the reducing agent—be it hydrogen or metal, or arsenious acid, for example—the primary product of the reduction of nitric acid is nitrous acid.

But these require the hypothesis, in opposition to facts, that silver is a very feeble basylous radical with a considerable affinity for oxygen, and this must therefore cause their rejection. Next, disregarding the evidence that the metal cannot substitute itself for the hydrogen of hydroxyl, the equations necessary to express the reaction will be found to be—

$$2Ag + 2HONO_2 = 2AgONO_2 + H_2 \quad (1)$$

$$\text{and } H_2 + HONO_2 = HOH + HNO_2 \quad (2)$$

$$\text{or, instead of (2), } H_2 + AgONO_2 = AgONO + H_2O \quad (3)$$

$$\text{and } AgONO + HONO_2 = AgONO_2 + HONO \quad (4)$$

in which hydrogen is assumed to be for a time at liberty. Hypotheses are further, therefore, here required to account for the non-appearance of any of the hydrogen, and for the non-production of ammonia. Then comes a difficulty in understanding why, as represented in (2), the hydrogen liberated, which must be chemically feebler than the silver which has displaced it, can separate and combine with the hydroxyl and nitroxyl of nitric acid, while the stronger silver fails to do so, as is contended upon this hypothesis. If instead of (2) the equations (3) and (4) are to be accepted, the deoxidation of silver nitrate must, against facts, be admitted to be easier than that of hydrogen nitrate, and the separation of oxygen and hydrogen to be easier than that of oxygen and silver. The deoxidation of silver nitrate by metallic silver would not be so difficult to admit as possible, but then the hydrogen of (1) would remain unaccounted for, and further we know (Divers, this Journal, 1871), on the contrary, that heated silver nitrite may become metallic silver and silver nitrate. Thus, from no point of view is the union of the metal with the oxygen probable, and therefore its union with the nitrogen of nitric acid becomes the more certain.

The reduction of the nitric acid by the silver class of metals seems not to pass beyond the formation of nitrites. The production of nitric oxide is accounted for by the well-known reaction between nitrous acid and water. The nitrous oxide produced when copper is dissolved in nitric acid alone is due, as already mentioned, to a reducing action of cuprous nitrate (copper and cupric nitrate) upon nitrous acid, as the investigations of Acworth and Armstrong have proved. Perhaps, too, the little nitrogen got in the same reaction is due to a similar reduction of the nitric oxide.

The metals of the tin-zinc class, characterised by forming ammonia with nitric acid, and hydrogen with hydrochloric acid, have certainly the power to displace the hydrogen of hydroxyl of such an acid as sulphuric acid, and thus may directly form nitrates by displacing the hydrogen of nitric acid. They differ from the silver class in possess-

ing this power, and consequently, in not forming nitrites from nitric acid directly. On the other hand they have the power, which metals of the silver class seem not to have, of forming nitrites from their own nitrates. When no other acid is present, there will be during the action both nitric acid and nitrate of the metal in the solution, and each undergoing its proper changes, one into hydrogen and metallic nitrate, the other into metallic oxide and nitrite. If a strong acid, such as hydrochloric or sulphuric acid, is present, this, by decomposing the nitrate, will prevent for the most part the secondary reaction by which nitrite is formed. But even in the absence of another acid only traces of nitrite are to be found in the acid solution instead of its abundance when silver or mercury is used, a result owing no doubt to a secondary reaction between hydroxylamine and nitrous acid, by which it is converted into nitrous oxide and water.

Respecting the separation of hydrogen from nitric acid by zinc and allied metals, it is known that with most metals this acid fails to give any free hydrogen. Acworth and Armstrong (*loc. cit.*) got it indeed by acting upon nickel, but convinced themselves that it was occluded hydrogen, and not derived from the nitric acid. In their case, no doubt they were right, judging from the evidence they adduce, although Gladstone and Tribe have since shown (this Journal, 1879), that occluded hydrogen may be completely oxidised by nitric acid. On the other hand the latter chemists have obtained a little hydrogen by throwing magnesium into nitric acid; but before admitting that this one metal may liberate hydrogen and others not, the possibility of this hydrogen coming from a reaction between water and magnesium, heated as these are by the nitric acid reaction, and coming just as hydrogen does from a mixture of sulphuric acid and nitric acid acting upon the zinc metals, should not be lost sight of until further experiments have been made. Although there is thus good reason to doubt whether nitric acid ever yields hydrogen actually free, the evidence afforded by the production of hydroxylamine and ammonia is nearly conclusive that the zinc metals do detach the hydrogen of nitric acid from its oxygen. The production of hydroxylamine could indeed, like the production of nitrites by the silver metals, take place without liberation of any hydrogen, by the metal uniting with both oxygen and nitrogen, and the resulting compound reacting with water to form hydroxylamine, thus :—

$$Zn(NO_2)_2 + 4Zn = Zn_2N_2O_2Zn + 2ZnO$$
$$\text{and } Zn_2N_2(O_2Zn) + 6H_2O = 2H_2N(OH) + 3Zn(OH)_2.$$

Such an action indeed may really take place when the metal is potassium or sodium, since these metals do form hydroxylamine and ammonia from their nitrates. But zinc, tin, and other members of

the class, though they form these products abundantly from nitric acid, either do not form them from their own nitrates at all or only to a slight extent, a fact inconsistent with the supposition of their direct action. It must therefore be admitted as probable that hydroxylamine is produced by the direct action of hydrogen, and not by the action of the metal.

In obtaining hydroxylamine from nitric acid the presence of a second acid has so very great an effect, that before proceeding further with the examination into the nature of the reduction with nitric acid, the nature of the reduction of the second acid had better be considered. One of its actions is to set the nitric acid free again as fast as it becomes metallic nitrate. Acting in this way it keeps the nitric acid under the influence of the metal until it is all destroyed, and at the same time prevents the formation of products of the reaction between the metal and its nitrate to a large extent, if not entirely. In thus decomposing the metallic nitrate, it also furnishes the additional hydrogen necessary for the production of hydroxylamine, that of the original nitric acid being only sufficient to convert one part out of seven into hydroxylamine—

$$7HNO_3 + 3Zn = H_3NO + 2H_2O + 3Zn(NO_3)_2,$$

and the change of the metal nitrate to hydrogen nitrate by the second acid, again allowing one-seventh of this to become hydroxylamine also, and so on to the end. It is generally assumed that the reducing effect of an acid and metal is due to their supplying hydrogen in the *nascent* state; but the account just given of what it would seem must happen in the case of nitric acid, is sufficient to show this assumption to be unnecessary. Deville indeed employed this very action of a mixture of sulphuric, or hydrochloric, and nitric acids upon zinc to disprove the hypothesis of the nascent state.* He gave an extensive table of the quantities of oxides of nitrogen, ammonia, and hydrogen yielded by different proportions of the acids acting upon zinc, and deduced from them that each acid pursued its action upon the zinc unaffected, except indirectly, by the presence of the other. Whatever hydrogen was liberated from the sulphuric acid escaped; and if no hydrogen escaped, or very little, this was due to the excess of nitric acid forming an envelope of zinc nitrate solution round the zinc, which neutralised the approaching sulphuric acid, and thus protected the zinc from its action. The formation of ammonia did not suggest to him any necessity for a supply of outside hydrogen to the nitric acid, because the ammonia was accompanied by that of oxides of

* I can at present speak of the contents of his papers (*Compt. rend.*, **70**, pp. 20 and 550) only from memory, as I have not seen them since the year in which they appeared, and have only preserved a reference to them in my note-book.

nitrogen, and therefore the hydrogen of the nitric acid might of itself be sufficient. His papers are imperfect, I consider, in their purpose of disproving the hypothesis of *nascency*, from the apparently insufficient explanation of the non-appearance of hydrogen when the nitric acid was in excess ; for until enough zinc had dissolved to neutralise the sulphuric acid present, hydrogen ought, on his explanation, to have been found among the gases. However that may be, there is, as I have explained, no need to resort to the hypothesis of nascent hydrogen to account for the transfer of the hydrogen of the second acid to the nitric acid in its transformation into hydroxylamine and ammonia.

In connection with this point I may refer to the experiment, recorded in the previous part of this paper, with zinc and sulphuric acid in very little water. In this experiment no hydrogen escaped, and yet much hydroxylamine and ammonia were formed from the nitric acid, from which it would seem that nascent hydrogen from sulphuric acid has nothing to do with the formation of hydroxylamine, since sulphuric acid of such a degree of concentration must be nearly inactive upon zinc. The experiments, the results of which I have tabulated, also serve, like Deville's, to show the improbability of nascent hydrogen from the sulphuric or hydrochloric acid being concerned in the formation of the hydroxylamine. For if this were the case, at least seven equivalents of one of these acids to one of nitric should have all its hydrogen taken up by the nitric acid,

$$3Zn + 7HCl + HNO_3 = H_3NOHCl + 3ZnCl_2 + 2H_2O,$$

and this is far from being so, hydrogen escaping. No escape of the hydrogen should be possible, considering the thorough commixture of the two acids as they come in contact with the zinc.

Another way in which the second acid acts is in preserving the hydroxylamine from destruction immediately upon its production. Thus, in keeping the solution free from metallic nitrate, it cuts off the source of nitrous acid, as already pointed out, and to that extent protects the hydroxylamine, so that while with the second acid present we get hydroxylamine, without it we get nitrous oxide, this oxide and water always resulting from the contact of nitrous acid and hydroxylamine. It may also be pretty safely accepted that hydroxyammonium chloride or sulphate is less sensitive to the action of both nitric acid and metal, than is the nitrate or the free base; for with the use of nitric acid alone and much diluted, most of the acid which suffers reduction becomes ammonia, very little becoming nitrous oxide, and ammonia is the product of the reduction of hydroxylamine by metals. This fact, too, the formation of much ammonia, serves to

show that it is not want of hydrogen from another source that prevents the finding of hydroxylamine when nitric acid alone acts on metals.

The use of the second acid, the hydrochloric or sulphuric acid added, appears then to be, not to take part in the reduction of the nitric acid, but to secure the reduction of all of it to hydroxylamine by supplying it with hydrogen in the way of double decomposition, and thus keeping it subject to the requisite reducing influence; and further to preserve it more or less from destructive influences when formed.

Nascent hydrogen from the second acid playing no part in reducing nitric acid, the action of the acid upon the metal is not wanted, and is further undesirable because it wastes acid and metal, and loads the solution with metallic salt. It is because of useless consumption of the second acid in dissolving zinc, that the calculated quantity of it—seven equivalents—is insufficient to secure the reduction of one of nitric acid, the excess required representing that part acting directly on the zinc with liberation of hydrogen. The greater effectiveness of sulphuric acid, recorded in the account of the experiments with zinc, is partly attributable to the fact that this acid acts more slowly than hydrochloric upon zinc, and remains therefore longer unsaturated at the service of the nitric acid. It is in part due, no doubt, to the fact of the slower action of this acid causing a less rise in temperature and consequent less destruction of hydroxylamine.

The superiority of one metal over another for the production of hydroxylamine is to be traced to this among other things, that it is less attacked by acids than the other metal. Thus tin has the advantage of being sufficiently basylous and very readily acted upon by nitric acid, without being very briskly acted upon by solution of hydrochloric or sulphuric acid. The destructive action upon hydroxylamine, however, of stannous chloride goes far to neutralise this advantage. A perfect metal for making hydroxylamine would be one readily acting upon dilute nitric acid and displacing its hydrogen, inactive upon sulphuric or hydrochloric acid, and inactive itself and giving a salt inactive upon hydroxylamine.

To resume now the long-deferred discussion of the nature of the change of nitric acid to hydroxylamine:—the conclusions already reached are, that the zinc-tin metals displace the hydrogen of nitric acid; that they do not themselves deoxidise it; and that the displaced hydrogen of one portion of nitric acid acts as the deoxidising and hydrogenising agent upon another portion of it. It may be admitted that this change takes place in successive stages, but it is doubtful whether there is any evidence of such a division of the reduction, while there are difficulties in reconciling their occurrence with the

attainment of the final result. Nitrous acid and hyponitrous acid, if present in the solution at all during the reduction, are so only in traces. The products of their reaction with hydroxylamine—nitrous oxide in the case of nitrous acid, and nitrogen (?) in the case of hyponitrous acid—appear also to be present only in traces when a sufficiency of the second acid is taken, and Kinnear (*loc. cit.*) finds all the nitric acid then as ammonia in the solution. The presence of a little nitrous oxide need not even be due to nitrous acid, but to a slight reaction between the metal and its nitrate, before the second acid can decompose it, generating nitrite, which then would act upon hydroxylamine. It seems more probable that, as a portion of nitric acid comes in contact with the metal, it is converted into hydroxylamine before giving place to a fresh portion of nitric acid, than that in contact with the metal there are portions of nitric acid in various stages of reduction. The change into hydroxylamine may indeed be a compound one, with its operations partly consecutive, partly simultaneous, but all occurring so close together as to be completed before the intermediate products can move out of the influence of the metal, and meet pre-formed hydroxylamine upon which to act. Or to view the change from another light, the action of the metal appears to be such that the nitric acid which has its hydrogen displaced does not suffer this change, independently of the other portion of the acid which takes up this hydrogen, but in connection with it. Admitting, however, that the change does take place in a succession of steps, it has still to be remembered that these are not necessarily, or even probably, the formation of nitrite and hyponitrite. In most chemical changes there are probably complex transition-bodies formed which then break up into the ultimate products; and in the present case it seems likely that nitrous acid, for example, if itself formed at all, passes next to a transition-body capable of decomposing to hyponitrous acid, but readily passing on directly to hydroxylamine, thus:

$$HNO_2 + 2H = HN(OH)_2 = HNO + OH_2,$$

or otherwise:

$$HN(OH)_2 + 2H = H_2NOH + OH_2,$$

a repetition of which action would give ammonia.

In considering the action of hydrogen upon nitric acid in stages, the combination of hydrogen with hydroxyl, and removal of its oxygen therefore from the nitrogen, must be regarded as preceding the attack upon either of the other oxygens, to hydroxylise which would be the first step in its removal. Thus, assuming the formation of nitrous acid, the reaction would be

$$HONO_2 + 2H = HOH + HNO_2.*$$

* To guard against a possible misconception, I may here add that in admitting

This seems to prove that the hydroxyl of hydroxylamine is not that of the nitric acid from which it was formed; and the conversion of ethyl nitrate to hydroxylamine leads to the same conclusion, the ethoxyl becoming replaced by hydrogen:

$$C_2H_5ONO + 2H = C_2H_5OH + HNO_2, \&c.$$

The theory of the nitronic constitution of nitrous acid also receives support here.

Hydrogen being the agent which reduces nitric acid to hydroxylamine, the greater activity of one metal over another in bringing about its production would furnish a difficulty, and such a difficulty Armstrong endeavours to meet by suggesting that the hydrogen is in the *nascent* state, with different degrees of *activity* determined by the metal which has liberated it. But as regards hydroxylamine, I am not at all sure that this difficulty does present itself. The quantity of hydroxylamine found in the solution is the difference between what has been formed and what has been destroyed. Besides its formation by the hydrogen of the reaction between nitric acid and metal, there may be its formation by the salt in solution, as in the case of tin (v. Dumreicher), but above all there may be its destruction by the salt in solution and also by the metal itself, as I shall endeavour to establish in the next paragraph. The varying results with different metals have apparently therefore sufficient explanation without attributing to the hydrogen different degrees of power.

While hydroxylamine appears to be formed by hydrogen which passes through the state of nitric acid, ammonia appears to be formed by the deoxidising action of the metal upon hydroxylamine; or, putting it in another way and going less beyond the facts, hydroxylamine results from one reaction, in which the metal attacks 7 mols. of nitric acid at a time, coming off with six nitrate radicals and leaving behind the hydroxylamine and water. Ammonia is formed in another reaction in which the metal attacks hydroxylamine and unites with it to form a compound afterwards decomposed by water or acid, as the circumstances may allow. That this is what takes place in the production of ammonia from hydroxylamine by reduction is to be seen in the fact that the change takes place not only in an acid solution, but also in a neutral or basic one in contact with the metal, and that, in the case of zinc at least, such a metallic compound actually occurs in the alkaline solution, and slowly decomposes into

the reduction of nitric acid to nitrous acid by hydrogen as perhaps occurring when the metal belongs to the zinc-tin class, I am not contradicting what I have said regarding the metals of the silver class. Of these I endeavour to prove, not that the hydrogen they might displace would not reduce nitric acid, but that they cannot displace hydrogen.

ammonia and metallic hydroxide. First, its formation may be thus represented—

$$Zn + H_2NOH = ZnH_2NOH,$$

and then the decomposition of the zinc ammonium hydroxide by water, thus:

$$ZnH_2NOH + H_2O = Zn(OH)_2 + H_3N.$$

As a matter of fact, while nitric acid passes direct as it were to hydroxylamine, there is a marked pause at the stage of hydroxylamine in its passage to ammonia, for otherwise that substance would not be found in such quantity. Now such a pause suggests a change in the method of attack, just such a one as that above indicated, and is fully accounted for in this way.

A peculiarity in the formation of hydroxylamine by aluminium demands notice. It is that hydroxylamine appears to form only or principally when the hydrochloric acid has been acting for some time, and has become nearly saturated. The experiments of Gladstone and Tribe, showing that this metal decomposes water in presence of aluminium chloride, render it very probable that in the formation of hydroxylamine this salt plays an important part, not, however, by causing the aluminium to act upon water, but to act much more freely upon nitric acid than it can otherwise do. This subject requires more examination. For the remarkable fact that magnesium forms hydroxylamine in presence of hydrochloric acid, but not in presence of sulphuric acid, I have no explanation to offer, except that perhaps its chloride, too, is in some way active.

As already described, the metal lead readily produces ammonia, but apparently not hydroxylamine. This fact can hardly be attributed to any high degree of activity in the metal as a reducing agent. It is probably to be accounted for in some way by its well-known special activity upon its own nitrate,* by its action upon water, or by its slow action upon acids, in consequence of the very slight solubility of its salts. The production of ammonia by iron, and not of hydroxylamine, is explained by the deoxidising action of ferrous salts. This is exerted even at common temperatures. A similar effect is exerted by stannous chloride in hot solution, and to a less extent in cold.

The experimental part of this paper is very incomplete, and the theoretical part of necessity, therefore, insufficiently supported by facts. Investigation of the subject is, however, now being continued in this laboratory, and will, I hope, not be interrupted until further results have been obtained. For great assistance with the experiments I am much indebted to Messrs. T. Fujii and T. Shimidzu, graduates of the Imperial Japanese College of Engineering.

* By this property lead shows relationship to the silver class of metals.

Summary.

Free nitric acid yields hydroxylamine when treated with tin, zinc, cadmium, magnesium, and aluminium. In presence of either hydrochloric or sulphuric acid the quantity obtained may be considerable, that is, at least, when the metal is either tin or zinc. Without a second acid only traces of hydroxylamine can be detected.

There is no reason to believe that the action of the hydrochloric or sulphuric acid upon the metal is instrumental in forming hydroxylamine. The second acid serves to decompose nitrate as fast as it is produced. In this way, (1) it holds the hydroxylamine in a state more stable than the nitrate; (2), it preserves the hydroxylamine from the destructive action of nitrous acid, by preventing that formation of this substance which would otherwise result from the reaction between a metal yielding hyroxylamine and its own nitrate; and (3), it determines the reduction of all the nitric acid to hydroxylamine by supplying the hydrogen for reproducing it, and so keeping it free to the last.

Metals act upon nitric acid in one of two ways, and are accordingly divisible into two classes. The one includes the metals silver, mercury, copper, and bismuth. The metals of this class form nitrite, water, and nitrate, and exert no further action, forming neither ammonia nor hydroxylamine. They do not convert their nitrate to nitrite. Their mode of action is to decompose the nitric acid into hydroxyl and nitroxyl, combining with these radicals to form hydroxide and nitrite, which, by secondary reactions, become water, nitrous acid, and metal nitrate. These metals therefore separate nitrogen from oxygen (hydroxyl) in decomposing nitric acid; they do not in this decomposition separate hydrogen from oxygen, just as they do not do so in any other case.

The other class of metals includes tin, zinc, cadmium, magnesium, aluminium, lead, iron, and the alkali-metals. These form ammonia and generally also hydroxylamine, but do not yield nitrite or nitrous acid with free nitric acid. On the other hand, they readily form nitrite by acting on their own nitrate. They exercise two actions, one upon the nitric acid itself, and one upon the hydroxylamine they have produced. They act first upon 7 mols. of the acid, separating, in the form of hydroxylamine, the hydrogen of six of them by forming nitrate, and leaving the seventh converted to water and the said hydroxylamine. This action occurs without evident break into successive stages. The second action of these metals is that in which they combine with hydroxylamine to form metal-ammonium hydroxide, which decomposes with water into metal hydroxide and ammonia.

Nitrites have a constitution indicated by the name "nitronates," that is, they have their metal directly united to their nitrogen. They have the same radical —NO_2— as nitrates have, these being its metaloxyl compounds.

LXII.—*On some Compounds of Phenols with Amido-bases.*

By Gibson Dyson, Dalton Scholar of Owens College.

Dale and Schorlemmer, in their recent investigation on the action of aqueous and alcoholic ammonia upon aurin, discovered the remarkable fact that it is extremely difficult to separate the aurin from the amido-bases formed, by means of dilute acids. Hence they were led to conclude that the aurin combined with the amido-bases, and they were able to confirm this view by the preparation of pure rosaniline aurinate (*Chem. Soc. J.*, 1883, **1**, 185).

Aurin being a phenol and rosaniline an amido-base, it appeared probable that analogous compounds of the phenols with different amido-bases might be obtained. A mixture in molecular proportions of phenol and aniline was therefore heated to the boiling point for a considerable time, and then left to cool. After some time large thin plates crystallised out, and finally the whole solidified to a crystalline mass. This, on recrystallisation either from alcohol or from petroleum-naphtha, yielded beautiful glistening plates melting at 29·5° (*loc. cit.*). At the request of Professor Schorlemmer I undertook the further investigation of these bodies and other compounds of phenols with amido-bases. The following are the results I have so far obtained:—

I. *Aniline Phenate*, $C_6H_5NH_2.C_6H_5OH$.

Dale and Schorlemmer describe the preparation of this compound, which they obtained by heating together molecular proportions of aniline and phenol to the boiling point; but it is also formed in the cold on standing. The product was purified by recrystallisation, either from alcohol or from petroleum-naphtha, and is thus obtained in well-defined crystals, the best being deposited from the last-named solvent.

These crystals closely resemble pure naphthalene in appearance, and when pure melt at 30·8°, and boil at 181° C. Dale and Schorlemmer

give the melting point 29·5° and the boiling point 184·5°, but their substance had been purified only by pressing.

Determination of the Aniline.—In order to determine the aniline in this compound directly, the following three methods were tried, but failed to give satisfactory results.

1. The aniline was precipitated as the double chloride of aniline and platinum by means of platinum tetrachloride. This method failed, in consequence of the reducing action of the phenol upon the double salt formed.

2. An excess of dilute hydrochloric acid was added to a weighed portion of the salt, and then the mixture was boiled until all the phenol had been expelled. The aniline hydrochloride left was next precipitated as the double salt by platinum tetrachloride, and the precipitate obtained was washed with a mixture of pure alcohol and ether. The results obtained, however, were considerably too low, this being probably due to the volatilisation of some of the aniline together with the phenol.

3. Varrentrapp and Will's method failed to give good results, since it was found impossible to prevent phenol or substances possessing a similar reducing action on the platinum double salt passing into the bulbs. The only method which promised to give accurate results was the determination of free nitrogen by Dumas' method, and subsequent experiments bearing out this promise, this method was adopted in the analysis of this compound, and also in similar determinations required in the course of the investigation.

The following analytical numbers were obtained :—

(a.) *Before recrystallisation, purified by Pressing only.*

	Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
(1.)	1·01425 grams	61·0 c.c.	7·51
(2.)	1·2025 ,,	69·6 ,,	7·23
(3.)	0·9535 ,,	60·0 ,,	7·97

Mean of the three determinations = 7·57 per cent.
Calculated = 7·48 per cent.

(b.) *After repeated recrystallisation from Petroleum-naphtha (boiling below 90°).*

Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
0·567 gram	34·4 c.c.	7·58

Found, 7·58 per cent. Calculated, 7·48 per cent.

The carbon and hydrogen, as obtained by combustion, were as follows:—

(1) substance, 0·213—CO_2 : 0·601—H_2O : 0·134.

	Calculated	Found.
Carbon.....	77·0 per cent.	76·9 per cent.
Hydrogen	6·95 „	6·99 „

(2) substance, 0·21—CO_2 : 0·5925—H_2O : 0·1325.

	Calculated.	Found.
Carbon.....	77·0 per cent.	76·9 per cent.
Hydrogen.....	6·95 „	7·01 „

II. *Toluidine Phenate*, $C_6H_4,CH_3,NH_2.C_6H_5OH$.

This compound was obtained by fusing together molecular proportions of paratoluidine and phenol; on cooling the mixture solidified to a soft mass, which was freely soluble in hot light petroleum-naphtha (b. p. below 90°). This solution was left to cool, whereupon it deposited well-formed needle-shaped crystals of the pure phenate, melting at 31·1°, some of which were from 2 to 3 inches in length. The following analytical results were obtained:—

Nitrogen.

	Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
(1.)	0·530 gram.	29·5 c.c.	6·94
(2.)	0·5235 „	29·5 „	7·04

Calculated, 6·99 per cent. of nitrogen.

Found, 6·99 per cent., mean of two determinations.

Carbon and Hydrogen.

Substance, 0·247—CO_2 : 0·704—H_2O : 0·173.

	Calculated.	Found.
Carbon.....	77·61 per cent.	77·69 per cent.
Hydrogen	7·46 „	7·76 „

III. *Naphthylamine Phenate*, $C_{10}H_7NH_2.C_6H_5OH$.

This body was obtained in a manner similar to that employed in the preparation of the aniline and toluidine phenates. By recrystallisation from light petroleum-naphtha (boiling below 90°) it is with difficulty obtained in well-formed needle-shaped crystals, possessing the characteristic smell of naphthylamine, and melting at 30·1°.

Nitrogen.

Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
1·587 grams	76·3 c.c.	6

Calculated, 5·9 of nitrogen. Found, 6 per cent. of nitrogen.

Carbon and Hydrogen.

Substance, 0·253—CO_2 : 0 7515—H_2O : 0·145.

	Calculated.	Found.
Carbon.....	81·01 per cent.	81·01 per cent.
Hydrogen	6·32 „	6·36 „

IV. *Aniline β-Naphthate,* $C_6H_5NH_2.C_{10}H_7OH$.

When pure β-naphthol and aniline are heated together in the proportions required by the above formula, a fibrous mass is obtained resembling crude naphthol in appearance. It is but slightly soluble in cold, but more freely so in hot petroleum-naphtha, from which it is deposited on cooling in the form of a crystalline powder, melting at 82·4°.

Nitrogen.

	Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
(1.)	1·099 grams	51·9 c.c.	5·9
(2.)	0·9745 „	45·5 „	5·83

Calculated, 5·9. Mean of two results, 5·86.

Carbon and Hydrogen.

(1) substance, 0·2035—CO_2 : 0·605—H_2O : 0·118.

	Calculated.	Found.
Carbon.....	81·01 per cent.	81·08 per cent.
Hydrogen	6·32 „	6·44 „

(2) substance, 0·221—CO_2 : 0·65925—H_2O : 0·1275.

	Calculated.	Found.
Carbon.....	81·01 per cent.	81·3 per cent.
Hydrogen	6·32 „	6·47 „

V. *Toluidine Naphthate,* $C_6H_4CH_3,NH_2.C_{10}H_7OH$.

This compound was obtained in exactly the same manner as the aniline naphthate, which it closely resembles in appearance.

It is a crystalline solid, melting at 80·8°.

Nitrogen.

	Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
(1.)	1·175	51·4 c.c.	5·46
(2.)	0·9295	43·9 „	5·89

Calculated = 5·57 per cent.
Mean of two determinations = 5·67 per cent.

Carbon and Hydrogen.

Substance, 0·1975 = CO_2 : 0·5885. H_2O : 0·121.

	Calculated.	Found.
Carbon	81·27 per cent.	81·31 per cent.
Hydrogen.....	6·77 „	6·8 „

VI. *Rosaniline Phenate*, $C_{20}H_{19}N_3.C_6H_5OH$.

If a mixture of rosaniline base and phenol, in the proportions required by the above formula, be dissolved in alcohol, and the solution allowed to evaporate slowly, a purple residue is obtained, exhibiting all the characteristic properties of a rosaniline salt.

I have not yet succeeded in obtaining this substance in the pure state, but an approximately pure compound may be obtained by employing the following method. A quantity of rosaniline is mixed with excess of phenol and heated. The product is dissolved in absolute alcohol, and the solution largely diluted with water, whereupon the rosaniline salt is partially precipitated, and completely so on standing, whilst the excess of phenol remains in solution. The precipitate is collected on a filter, redissolved in alcohol, and once more reprecipitated from this solution by excess of water, filtered off, and dried at a low temperature. The compound thus obtained is not chemically pure, as will be seen from the following analysis:—

Carbon and Hydrogen.

Substance, 0·16—CO_2 : 0·46—H_2O : 0·093.

	Calculated.	Found.
Carbon	78·98 per cent.	78·4 per cent.
Hydrogen	6·32 „	6·26 „

The above discrepancies may be easily accounted for by the fact that the rosaniline base used in the experiments was not pure, as the commercial article contains in all probability an admixture of the para-compound.

When a solution of rosaniline phenate is treated with an alkali, a fine blue coloration is produced, which disappears on addition of an acid, but is restored on again making the solution alkaline. This remarkable reaction is probably due to the presence of some other compound in the rosaniline salt, and it will be interesting to ascertain whether this impurity would also be formed in the case of pure rosaniline being used in the preparation of the rosaniline phenate.

VII. *Xylidine Naphthate.*

A mixture of isoxylidine and β-naphthol, in the proportions of their respective molecular weights, was heated until a uniform liquid was formed, which was then left to cool. The semi-solid magma thus obtained was exhausted with hot light petroleum, in which it is freely soluble, and the solution was left to crystallise. The analysis of the crystals obtained gave the following results:—

Carbon and Hydrogen.

Substance, 0·177—CO_2 : 0·935—H_2O : 0·0945.

	Calculated.	Found.
Carbon.....	81·5 per cent.	82·42 per cent.
Hydrogen.....	7·169 „	5·9 „

From the above analysis it would appear that the treatment with the hot spirit had simply extracted the xylidine from the substance, and in order to confirm this assumption, the substance was redissolved in hot petroleum-naphtha, and the crystals obtained on cooling were carefully dried and analysed.

Carbon and Hydrogen.

(1) substance, 0·1605—CO_2 : 0·4885—H_2O : 0·0795.

	Calculated.	Found.
Carbon.....	81·5 per cent.	83·0 per cent.
Hydrogen	7·169 „	5·502 „

(2) substance, 0·238 — CO_2 : 0·725 — H_2O : 0·120.

	Calculated.	Found.
Carbon.....	81·5 per cent.	83·06 per cent.
Hydrogen	7·169 „	5·58 „

Now as xylidine contains 79·3 per cent. of carbon, and naphthol 83·3 per cent., we have $x + y = 100$.

$$79{\cdot}3x + 83{\cdot}3y = 83 \times 100$$

$y = 92{\cdot}5$ per cent. $y = C_{10}H_7OH$.

Hence the substance was nearly pure naphthol.

I next tried to obtain the salt by heating β-naphthol with excess of isoxylidine, and leaving the mixture to cool and crystallise. The excess of xylidine was then removed by washing with cold light petroleum-naphtha, and the crystalline residue analysed.

Carbon and Hydrogen.

Substance, 0·2595 — CO_2 : 0·7787 — H_2O : 0·16.

	Calculated.	Found.
Carbon	81·5 per cent.	81·8 per cent.
Hydrogen	7·169 „	6·85 „

The above numbers again clearly show that the substance was either a mixture, or else a highly unstable compound.

VIII. *Rosaniline Aurinate*, $C_{20}H_{19}N_3—C_{19}H_{14}O_3$.

The preparation of this salt has already been referred to in the introduction to this paper. I have since succeeded in obtaining it in moderately large crystals possessing a fine beetle-green lustre. These crystals belong to the hexagonal system, and exhibit chiefly the form of a short prism and base ∞P . 0P.

IX. *Aniline Aurinate*, $C_6H_5NH_2.C_{19}H_{14}O_3$.

On dissolving molecular proportions of aniline and aurin in alcohol, and evaporating at a moderate temperature, a red crystalline residue is obtained, soluble in alcohol, imparting to it an orange colour.

It dyes silk in neutral solutions exactly the same shade as aurin. As the quantity of pure aurin at my disposal was very small, the further investigation of this compound had to be postponed.

LXIII.—*Chemistry of Lacquer (Urushi).* Part I.

Communication from the Chemical Society of Tokio.

By Hikorokuro Yoshida.

I have lately, through the kindness of Mr. Magaribuchi, had an opportunity of examining the chemical properties of Urushi in its pure form, as well as of ascertaining the nature and properties of the various substances with which it is decomposed, when it exudes as juice from the tree.

At present much importance attaches to this substance in conse-

quence of its many peculiar and excellent qualities, and its increasing application to useful purposes; I have thought therefore that a correct account of its chemical nature would possess some interest.

The specimen I understood had been obtained from Yoshino, in the province of Yamato, and was very nearly in the state in which it came from the tree; it had been altered simply by the formation of a thin crust of hardened urushi on the surface of the juice contained in the bottle. I might also add that, as the juice was originally intended for chemical investigation, and as it was collected in the best place in the empire, and under strict official inspection, it must have been in the purest form obtainable.

When Mr. Magaribuchi gave me the substance and also subsequently, he communicated his observations upon it, which, with others of my own, form the present paper.

I have here to give my sincerest thanks to Mr. O. Korschelt with whose kind counsel I had the pleasure of working the subject in the Chemical Laboratory of the Imperial Geological Survey, and also to Mr. J. Sakurai who helped me in various ways in preparing the present communication.

Urushi is the milky secretion of *Rhus vernicifera*, and is the material for the well-known Japanese lacquer varnish. The tree is cultivated in many parts of the country, throughout almost all latitudes, *e.g.*, at Dewa, Aizu, Hiroshima, and in many places about Tokio; the best urushi, however, is obtained at Yoshino. The tree is very similar in aspect to the ordinary wax-tree, and attains the height of 9—12 feet; trees about fifteen years old yield the largest amount of the juice. Two sorts of the juice are generally obtained from a tree, and by different processes; they are distinguished as ordinary "Ki-urushi" and "Seshime-urushi."

Ki-urushi (or raw lacquer) is the better of the two, and is collected best in June by making shallow cuttings in the stem of the tree, when it exudes as drops from between the outer and inner barks. A single tree yields on an average about $2\frac{1}{2}$ grams of this kind of juice. Branches and twigs of the tree, some of which are usually cut down each year, when steeped in water for some months and afterwards warmed in the fire, give out an inferior kind of juice; this is seshime-urushi, which is used as under varnish after being mixed with some drying oil.

The juice is never sent to market in the form in which it comes from the tree, but is usually mixed with more less of what is called "Mokuyiki"* (literally wood-juice), *e.g.*, what is ordinarily called

* Mokuyiki is a substance much resembling ordinary urushi in appearance; it contains about 15 per cent. of the substance insoluble in alcohol, in which gum is present in large quantity. I have not yet been able to make a close examination of

Yoshino. Urushi consists of 60 per cent. of the genuine juice with 40 per cent. of mokuyeki, whilst the inferior quality contains as much as 70 per cent. of the latter substance. Further in the hands of varnish makers, some quantity of linseed oil is generally added to the already mixed juice, which, if excess is avoided, does not much impair the drying power of urushi.

Different colours are imparted to urushi by the addition of body pigments, such as lamp-black, vermillion, indigo, orpiment, &c.; thus red lacquer is prepared with 20 parts of linseed oil, 70 parts of urushi juice, and about 10 parts of vermillion, &c. Such is a rough yet general account of the extraction and preparation of urushi juice for varnish-making, but those who desire to get detailed information on this part of the subject, will find a full and accurate account in the writings of Mr. Quinn, English Consul at Hakodate. The pure and unaltered urushi is a thick greyish fluid of dextrinous consistence, which under the microscope is found to consist of minute globules, some of darker, the others of lighter colour, mixed with small particles of opaque brownish matter, the whole being held mixed in the form of intimate emulsion. It has a characteristic sweetish odour, and sp. gr. 1·0020 (20° C.); some specimens, such as that obtained from Hachiôji, contained a good deal of bark-dust and other impurities which raise it sp. gr. as high as 1·038. If the juice be exposed to moist air in a thin layer at about 20°, it rapidly darkens in colour and *dries up to a lustrous transclucent varnish.* It contains a small quantity of volatile poison, which acts terribly on some persons, producing very disagreeable itching.

Mr. S. Ishimatsu, in a paper on urushi, written some years ago at Tokio University, and afterwards communicated to the Manchester Philosophical and Literary Society by Professor Roscoe (Feb. 18th, 1879), has shown that the constituents of urushi are a resin, a gum, water, and a small quantity of residue insoluble in water and in alcohol.

The method of separation of these substances which I pursued was the same as that adopted by Mr. Ishimatsu, thus:—

A resinous acid, together with a small quantity of the volatile poisonous body, is separated from the other substances in the juice by treating it with absolute alcohol, evaporating the solution, and drying the acid at 105—110°.

The residue is boiled for some time with water, and the water extract evaporated on a water-bath till it acquires a constant weight. This gives the quantity of gum.

the substance, but I think that it is in all probability a very impure form of the urushi juice.

The final residue, consisting chiefly of a coagulated diastatic matter, with very small quantities of cellulose and insoluble colouring matter, is dried at 100°, and weighed as such.

The difference of the sum of numbers from 100 gives the amount of water and volatile matter. Thus pure Yoshino urushi consisted of—

	Per cent.
Part soluble in alcohol (urushic acid)	85·15
Gum arabic	3·15
Residue (diastatic matter)	2·28
Water and volatile matter	9·42
	100·00

Pure urushi does not, I think, vary much in composition, but as I have already remarked, it is usually mixed with varying quantities of mokuyiki, and it is natural to suppose that such a mixture will rarely show identity in composition. Thus Mr. Ishimatsu gives the following as a mean result of two experiments made on a sample bought at Tokio:—

	Per cent.
Part soluble in alcohol.....	58·24
Gum	6·32
Residue	2·27
Moisture and other volatile matter....	33·17
	100·00

In the Hachiôji sample, which must have contained some quantity of mokuyiki, I have found the amount of gum and diastatic matter very much higher (about 12 per cent.), and the proportion of urushic acid much lower than those indicated in the analysis of a Yoshino specimen.

1. *Examination of the Alcoholic Extract:—Urushic Acid and Volatile Poison.*

A peculiar acid, which I now call *urushic acid*, is the main constituent of the original juice, as well as of the portion soluble in alcohol. The juice also contains a very small quantity of a volatile poisonous body, which also passes into alcoholic solution, being almost completely driven out during the drying of the acid at 105—110°. It is a pasty substance of somewhat dark colour, having the characteristic smell of the original juice, readily soluble in benzene, ether, carbon bisulphide, less easily in fusel oil and petroleum of high-boiling point, completely insoluble in water. Its sp. gr. taken at 23° is 0·9851;

it remains unchanged at 160°, and above 200 decomposes slowly with carbonisation. Exposed to the air, it *neither dries up*, nor *shows any sign of change as the original juice does*, and in other respects it is a very stable body. From the alcoholic solution of the acid many metallic salts can be produced, most of which are slightly soluble in alcohol, but almost insoluble in water.

Silver nitrate gives at first a fine dark precipitate moderately soluble in alcohol; on boiling, silver is reduced, with deposition of a mirror on the sides of a vessel.

Platinic chloride gives a gelatinous black precipitate, somewhat soluble in alcohol; on standing, the precipitate sinks down, and ultimately coheres to a pasty mass.

Gold chloride and acetate of uranium give very fine dark brownish precipitates, behaving like the precipitate obtained with platinic chloride.

Nitrate of copper imparts a black colour to the alcoholic solution of the acid; if it be considerably diluted with water, the copper salt separates out in the most finely divided state.

The acid dried at 110° and analysed gave the following numbers:—

I. 0·8226 gram substance gave 2·3690 grams CO_2 and 0·6871 gram H_2O.

II. 0·4235 gram substance gave 1·1995 gram CO_2 and 0·3334 gram H_2O.

	I.	II.	Theory for $C_{14}H_{19}O_2$.	Theory for $C_{14}H_{18}O_2$.
Carbon	77·09	77·01	76·71	77·06
Hydrogen	9·28	8·75	8·67	8·28
Oxygen	13·63	14·24	14·62	14·66
	100·00	100·00	100·00	100·00

Acetate of lead gives a greyish flocculent precipitate, which is a very characteristic reaction of the acid; a quantity of this compound was prepared, as in Mr. Ishimatsu's experiments, by precipitating an alcoholic solution of the acid with acetate of lead. The precipitate was first washed with alcohol, then with well boiled water, first dried over a water-bath, and finally over sulphuric acid in a desiccator, and analysed.

I. 0·7236 gram substance gave 1·3818 gram CO_2 and 0·3478 gram H_2O.

II. 0·5021 gram substance gave 0·1765 gram PbO. Pb = 32·63 per cent.

III. 0·6020 gram substance gave 0·2093 gram PbO. Pb = 32·27 per cent.

	Per cent.	Theory for $(C_{14}H_{17}O_2)_2Pb$.
Carbon	52·08	52·40
Hydrogen	5·34	5·30
Oxygen	10·43	10·01
Lead	32·45	32·29
	100·00	100·00

This lead compound is a somewhat unstable body; when heated to 100° in an air-bath, it gives out a peculiar odour and turns darker in colour; at 110—115° it melts to a dark brownish mass, and at about 120° it ignites spontaneously in the air, burning with smoky flame, and leaving an oxide of lead.

Another salt of this acid I examined was an iron compound. Ferric chloride gives a deep black voluminous precipitate, very sparingly soluble in alcohol, and almost insoluble in water. A quantity of the alcoholic solution of the acid was precipitated with an insufficient amount of ferric chloride, with the view of seeing whether this fractional precipitation gives a salt of different composition; the compound obtained, however, proved to be a salt of very acid nature, as will be seen below; it was first dried over a water-bath, and then over sulphuric acid, and analysed.

I. 0·5000 gram substance gave 1·03644 gram CO_2 and 0·3680 gram H_2O.

II. 0·5000 gram substance gave 1·3640 gram CO_2 and 0·3662 gram H_2O.

III. 0·7890 gram substance gave 0·0234 gram Fe_2O_3.

	I.	II.	$(C_{14}H_{17}O_2)_3Fe + 9(C_{14}H_{18}O_2) + 2H_2O$.
Carbon	74·42	74·40	74·53
Hydrogen	8·18	8·13	8·03
Iron	2·07	2·07	2·08
Oxygen	15·33	15·40	15·38
	100·00	100·00	100·00

Another preparation of iron salt was made, using a larger quantity of ferric chloride than before; the compound again proved to be another acid salt, but of less complexity than that above indicated; on analysis it gave the following numbers:—

I. 0·5000 gram substance gave 1·3660 gram CO_2 and 0·3670 gram H_2O.

II. 0·6968 gram substance gave 0·0428 gram Fe_2O_3.

		Theory for $(C_{14}H_{17}O_2)_3Fe + 3(C_{14}H_{18}O_2)$.
Carbon	74·56	74·06
Hydrogen	8·16	7·72
Iron	4·29	4·11
Oxygen	13·59	14·11
		100·00

Both these iron salts have very similar characters; they are light substances of a faint peculiar odour. At 105—110° they melt to a black mass with some decomposition, and at a somewhat higher temperature ignite spontaneously, giving out dense smokes of peculiar odour.

It is owing to the formation of some of these iron compounds, I think, that practical lacquermen carefully avoid the use of iron instruments in dealing with urushi; I have found experimentally that a small quantity of iron rust rubbed with urushic acid at once imparts a dull black colour to the substance.

Free alkalis impart a very dark colour to the solution of this acid, which looks purplish-blue by transmitted light, and very dark brown by reflected light. If exposed to the air, this viscid compound rapidly blackens and dries up; it is a compound of an alkali-metal with the acid, the normal salts of which will probably be represented by the formula $C_{14}H_{17}MO_2$; the substance, however, was not quite fit for analysis, as it was very difficult to purify. It is soluble in a rather large quantity of ether or benzene, and less easily in water and alcohol.

Sulphuric acid apparently produces no change in this black compound, but if boiled with very strong hydrochloric acid, it is converted into an elastic gummy substance, which I shall describe more particularly when I come to speak about the action of hydrochloric acid upon urushic acid. The solution of this alkali compound in light petroleum oil gives an excellent lustrous varnish, which dries up very easily.

Soluble salts of mercury, zinc, nickel, cobalt, manganese, and those of earthy metals do not give any distinctive reaction with urushic acid.

Bromine acts powerfully upon urushic acid, evolving fumes of hydrobromic acid.

To a solution of the acid in carbon bisulphide bromine was gradually added till it was in some excess; the whole was evaporated to dryness over water-bath; the mass exhausted with strong alcohol; and the extract again evaporated, whereupon it yielded a dark semi-solid mass. This was examined for bromine by ignition with pure lime: 0·7060 gram substance gave 1·1510 gram AgBr or Br = 69·37

per cent., agreeing nearly with a hexbromo-derivative of the acid, viz., $C_{14}H_{12}Br_6O_2$, which requires 69·36 per cent. bromine.

At ordinary temperatures it is almost a solid body, of a brownish colour, and soluble in most solvents of urushic acid; by using regulated quantities of bromine, its lower substitution products might perhaps be obtained. Chlorine also gives a series of substitution products, but the compounds have not yet been fully examined; they will be described in a later communication.

The distillation of urushic acid with lime did not yield any definite results. The decomposition appears to be very complicated, and some oxygenated bodies are still present amongst the products, contrary to the expectation that a hydrocarbon would be obtained corresponding to the original acid. It should be observed, however, that these lower fractions, which are free or nearly so from oxygenated bodies, approach the composition $C_{14}H_{24}$, probably one of the higher hydrocarbons of the terpene series. They are nearly colourless light oils of a peculiar odour, somewhat recalling that of borneene; they absorb oxygen from the air and resinise; they unite readily with bromine, and are blackened by concentrated sulphuric acid in the cold.

Long-continued action of strong hydrochloric acid upon urushic acid produces a peculiar change in the latter, the resulting body having exactly the same composition as the original acid, but very different properties. A quantity of urushic acid was heated with a very large excess of strong hydrochloric acid for about three days, the acid lost by evaporation being replaced. Urushic acid under this treatment first swells up to a soft sponge, gradually assumes a caoutchouc-like state, and finally hardens to a dark non-adhesive mass. The substance was cut up into small pieces, boiled with water, filtered,* and dried over a water-bath till the last trace of hydrochloric acid retained in the pores of the substance had been expelled. On cohobation with alcohol, a small quantity of the substance dissolved, which on examination showed the usual characters of unchanged urushic acid. The residue dried at 105°, and analysed, gave the following numbers. No chlorine was found in the substance:—

0·4022 gram substance gave 1·1360 gram CO_2 and 0·3356 gram H_2O.

	Found.	Mean number obtained for urushic acid.
Carbon	77·07	77·05
Hydrogen	8·77	9·01
Oxygen	14·16	13·94
	100·00	100·00

* The filtrate left no residue on evaporation.

It appears from this that urushic acid suffers molecular transformation (polymerisation) under the influence of strong hydrochloric acid. β-urushic acid thus formed is a dark brownish solid body, having a faint peculiar odour, and is soluble in the usual solvents of urushic acid.

As such was the case, an experiment was tried to ascertain whether urushic acid dries in an atmosphere charged with hydrogen chloride. A glass plate very thickly coated with pure urushic acid placed upon a basin containing fuming hydrochloric acid under a bell-jar, dried after standing for about two days. The urushic acid darkened in colour on drying, and looked somewhat similar to the naturally dried lacquer. Strong nitric acid has no action upon β-urushic acid, even on boiling, though it acts very powerfully upon urushic acid; when the β-acid is heated to 100° it merely softens a little, and even at 130° it shows no sign of decomposition. It appears that the substance obtained by the decomposition of an alkali salt of urushic acid with hydrochloric acid is the same body as β-urushic acid.

The action of strong nitric acid upon urushic acid gives rise first to a series of nitro-substitution products, which appear to change afterwards into another acid containing a larger number of oxygen-atoms. The reaction is very energetic, the urushic acid first swelling up to about thirty times its original bulk in the form of a yellowish sponge, which disappears gradually with the progress of the reaction. A quantity of this porous body was collected after about half a day's heating, treated with a larger quantity of water, and then dissolved in alcohol, and an iron compound precipitated from it with ferric chloride. The substance, after the usual purification and drying, was analysed, and the following numbers were obtained:—

I. 0·5031 gram substance gave 0·9498 gram CO_2 and 0·2183 gram H_2O.

II. 0·3802 gram substance gave 27·5 c.c. nitrogen at 23° and 784 mm. P.

III. 0·4139 gram substance gave 0·0578 gram Fe_2O_3.

		Theory for $(C_{14}H_{15}(NO_2)_2O_2)_3Fe$.
Carbon	51·49	51·59
Hydrogen	4·82	4·61
NO_2	28·16	28·25
Iron	9·77	9·81
Oxygen	5·76	5·74
	100·00	100·00

This is the iron salt of *dinitrourushic acid.*

The original acid is a bright yellowish solid, readily soluble in the usual solvents of urushic acid, and gives characteristic reactions with many metallic salts; those of silver, lead, zinc and manganese are light yellowish precipitates, of copper and iron greenish-yellow, and of soda and potash brownish. The acid itself and its metallic salts are to some extent soluble in water, and more soluble in alcohol.

The higher nitro-substitution products, which are likewise yellowish solid substances, and also their salts, are characterised by their greater solubility in water and alcohol. The other properties of these, as well as those of the product of the final action of nitric acid upon urushic acid, are now being studied.

We are not yet acquainted with the chemical nature of the volatile poisonous substance which passes into alcoholic solution, together with urushic acid from the juice. It comes over with water in the form of a thin oily film when a quantity of the juice is distilled; the distillate reduces solution of mercuric chloride, but does not give any precipitate with acetate of lead; it is almost impossible to do anything with it unless very large quantities of the juice are operated upon.

2. *Examination of the Water Extract—the Gum.*

Gum is another normal constituent of urushi, and forms 3—8 per cent. of the original juice.

As gum is insoluble in alcohol, it is conveniently separated by treating that portion of the original juice insoluble in alcohol with boiling water, filtering, and finally evaporating the aqueous solution of gum over the water-bath till the weight of the substance remains constant. In this way a friable light-coloured substance is obtained, tasteless and inodorous; this is the anhydrous gum. On combustion it gave the following numbers:—

0·5267 gram substance gave 0·7823 gram CO_2 and 0·2834 gram H_2O, and 0·0267 gram ash.

Analysis of the ash in a separate sample of the substance gave the following:—

	Per cent.	
Silica	0·48	
Alumina	7·85	
Lime	44·77	
Magnesia	5·79	
Potash	13·68	
Soda	1·33	
Carbonic acid	26·10	(by difference)
	100·00	

If the metals in the ash be replaced by the equivalent amount of hydrogen, and the result calculated for carbon, hydrogen, and oxygen, the above numbers will give—

		Arabic acid, ($C_{12}H_{22}O_{11}$).
Carbon	42·47	42·11
Hydrogen	6·40	6·43
Oxygen	51·13	51·46
	100·00	100·00

Mr. Ishimatsu's analysis of the gum is as follows. In it, however, no mention is made of the quantity and nature of the ash:—

	Per cent.
Carbon	41·37
Hydrogen	6·55
Oxygen	52·08
	100·00

The gum when inverted has the power of reducing Fehling's solution.

0·4747 gram substance (ash deducted) after inversion with 10 per cent. hydrochloric acid and precipitated gave 0·8114 gram CuO.

If we suppose that after the hydration, 1 mol. of arabic acid ($C_{12}H_{22}O_{11}$) changes into 2 mols. of $C_6H_{12}O_6$, the molecular ratio which the product of inversion, be it glucose or arabinose, bears to cupric oxide will be 1 : 5, exactly the same as that of dextrose to CuO, and consequently its cupric oxide reducing power, or K, will be 100. These facts leave no doubt as to the identity of the gum in urushi with the essential constituent of gum arabic; it is present in urushi in the form of acid salts of arabic acid, chiefly of potash, lime, alumina, and magnesia, and the only point of difference which is probably of interest is the presence of an alumina salt, which has not hitherto been observed in other gums.

A mixture of gum and urushic acid (and with water) in the proportion in which they exist in the juice, does not undergo any change whatever, even when exposed to the condition most favourable for the drying of the lacquer. Moreover part of the gum can be extracted in an unchanged state from the once perfectly dried lacquer; and since it exists in the original juice in the form of aqueous solution, it probably serves to keep the constituents of the juice in a state of uniform distribution and intimate emulsion. It may also act as a binding material, and assist the adhering power of the lacquer when laid upon any surface.

3. *The Diastatic Matter and its Action upon Urushic Acid.*

That portion of the juice which remains insoluble in alcohol and boiling water, consists chiefly of a nitrogenous substance, the action of which upon urushic acid has been ascertained to be the cause of the drying of the lacquer. It forms 3—8 per cent. of the original juice, that which contains it in larger proportion having the property of drying more quickly, while such a lacquer gives a varnish with inferior lustre.

The substance, as separated from the gum by the usual method of boiling with water, has no action upon urushic acid, but the residue itself (after the separation of urushic acid), or its extract with cold water, shows that peculiar diastatic activity in an unimpaired degree; when such a solution is boiled, the albuminoïd coagulates in the form of a white precipitate.

The substance dried first over water-bath and then over sulphuric acid, and analysed, gave the following numbers:—

I. 0·5008 gram substance gave 1·1610 gram CO_2, 0·3336 gram H_2O, and 0·0060 gram ash.

II. 1·0000 gram substance gave 0·6360 gram $(NH_4)_2PtCl_6$.

Carbon	63·44
Hydrogen	7·41
Nitrogen	4·01
Oxygen	22·94
Ash	1·20
	100·00

In the ash small quantities of sulphur and phosphorus were detected.

It differs from other vegetable albuminoïds in containing a notably smaller amount of nitrogen; the latter, as well as the active principles of the diastase (malt), koji, and saliva, do not possess the same property of exerting the peculiar action above-mentioned upon urushic acid.

Two series of experiments were instituted to test the activity of the diastatic matter upon urushic acid, first at different temperatures in the air, and secondly under different gaseous media.

For this purpose, a small quantity of the original juice was put into a covered breaker and subjected to the regulated heat of a water-bath, a small quantity of water lost by evaporation from the juice being afterwards replaced by approximately the same amount.

The heated juice was next very thinly coated on a glass plate and left to dry in a box, the air of which was kept constantly moist by the falling in of the drops of water. The time of heating the juice

was, in each experiment, $3\frac{1}{2}$—4 hours, and the temperature of the drying box was 20°.

1. At ordinary temperature (20°) the sample dried after $3\frac{1}{2}$ hours in air, and the same under a bell-jar containing moist oxygen dried after less than 2 hours.
2. Heated at 30°, the sample dried after 4 hours.
3. Heated at 40—43°, the sample dried after $4\frac{1}{2}$ hours.
4. Heated at 50°, dried, time not known.
5. Heated at 55—59°, almost dried after 24 hours; the surface of the lacquer had a dull appearance.
6. Heated at 60—63°, did not dry.
7. Heated at 80°, did not dry.
8. Heated at 100°, did not dry.

Next, a glass plate similarly coated with urushic juice was put under a bell-jar containing an experimental gas, and left to dry at the temperature of the surrounding air, which at this time ranged between 13—15°.

1. In dry air, the sample did not dry.
2. In moist air, the sample dried after 4 hours.
3. In dry oxygen, the sample did not dry.
4. In moist oxygen, the sample dried after $2\frac{1}{2}$ hours.
5. In dry hydrogen, the sample did not dry.
6. In wet hydrogen, the sample dried after $1\frac{1}{2}$ days.
7. In dry carbonic acid gas, the sample did not dry.
8. In wet carbonic acid gas, the sample dried very slowly after 2 days.
9. In dry nitrogen, the sample did not dry.
10. In wet nitrogen, the sample dried after $1\frac{1}{2}$ days.

The most legitimate inference to be drawn from all these experiments, is that the combination of oxygen and moisture at the temperature of 20°, or thereabouts, is an essential condition for the display of the fullest activity of the diastase, and consequently most favourable for the drying of the lacquer; with increase of temperature the drying power diminishes, until at 63—63° the substance entirely loses its activity; this is then the point at which the coagulation of the albuminoïd takes place, or, in other words, the diastatic matter dies. With other gases, however, I am inclined to think that a small quantity of atmospheric air, which may have been present in them, might have favoured the condition for drying, which otherwise could not have been possible.

These conclusions bear out the practical experience of our lacquer men, viz., that lacquer dries best in the rainy reason; it dries better

in summer than in winter—a damp atmosphere of about 20—30° being just the state of air during the rainy season of a year.

The question still remains to be asked, How does the diastase act upon urushic acid, or what is the change which the urushi juice undergoes on drying? To solve this question, the states of the lacquer, before and after the drying, have been examined and compared.

A quantity of the fresh juice was rapidly heated over the water-bath so as to coagulate the albuminoïd and put a stop to its further action upon urushic acid. After continuing the heat, so as to expel all the water from the juice, it was analysed and gave the following numbers:

I. 0·4090 gram substance gave 1·1318 gram CO_2 and 0·3290 gram H_2O.

II. 0·4213 gram substance gave 1·1679 gram CO_2 and 0·3420 gram H_2O.

III. 2·0540 grams substance gave 0·0359 gram $(NH_4)_2PtCl_6$.

IV. 2·1564 grams substance gave 0·0046 gram ash.

	I.	II.	Mean.	Numbers calculated from the constituents of the juice.
Carbon....	75·47	75·61	75·54	75·54
Hydrogen	8·93	9·01	8·97	9·14
Nitrogen ..	—	—	0·11	0·10
Ash	—	—	0·21	0·21
Oxygen ...	—	—	15·17	15·01
			100·00	100·00

The lacquer dried (hardened) in the usual manner, and afterwards heated at 100°, has the following composition:—

I. 0·5434 gram substance gave 1·4124 gram CO_2 and 0·4186 gram H_2O.

II. 0·4608 gram substance gave 1·1970 gram CO_2 and 0·3276 gram H_2O.

III. 2·1215 grams substance gave 0·0310 gram $(NH_4)_2PtCl_6$.

IV. 1·1717 gram substance gave 0·0043 gram ash.

	I.	II.	Mean.
Carbon	70·91	70·84	70·85
Hydrogen....	8·55	7·90	8·22
Nitrogen	—	—	0·092
Ash	—	—	0·032
Oxygen.....	—	—	20·52
			100·00

The comparison of the results of these two sets of analyses indicates that the lacquer in hardening had taken up oxygen, and we see that, other things remaining the same, the amount of oxygen thus taken up is very nearly accounted for on the supposition that each molecule of urushic acid, $C_{14}H_{18}O_2$, in the juice, has taken up 1 atom of oxygen, and changed into another body of the formula $C_{14}H_{18}O_3$.

Further proof of this theory has been arrived at by the isolation of pure *oxy-urushic acid* ($C_{14}H_{18}O_3$), which showed all the properties of a dried lacquer.

Urushic acid was subjected to the action of strong chromic acid mixture (which contains some excess of sulphuric acid, so as to prevent the precipitation of chromic hydrate). The product cohobated with absolute alcohol for some time to dissolve away the unacted urushic acid, gave, on drying (at 105°), a brownish powder having the following composition:—

I. 0·3059 gram substance gave 0·8021 gram CO_2 and 0·2296 gram H_2O.

II. 0·4245 gram substance gave 1·1134 gram CO_2 and 0·3103 gram H_2O.

	I.	II.	Mean.	Theory for $C_{14}H_{18}O_3$.
Carbon	71·55	71·50	71·52	71·79
Hydrogen ..	8·32	8·13	8·23	7·69
Oxygen	—	—	20·25	20·52
			100·00	100·00

This substance is very stable, and resists the action of strong boiling nitric acid; no solvent has yet been found for it.

An attempt was also made to estimate the quantity of carbonic acid evolved during the drying of the lacquer. It was found that this quantity is so small as not to affect the general result in any sensible degree. Thus, 1·5 gram of the juice gave out 0·0036 gram CO_2 (= 0·24 per cent.) during its hardening in an atmosphere of moist oxygen, which was completed at the end of two hours. I am inclined to attribute this phenomenon to the decomposition of a small quantity of gum (= 0·0085 gram in this case) by the diastase, simultaneously with its action upon urushic acid.

The results, so far arrived at, may be summed up in the following statement:—

Urushi juice (lacquer) consists essentially of four substances, viz., urushic acid, gum, water, and a peculiar diastatic matter; and the phenomenon of its drying is due to the oxidation of urushic acid, $C_{14}H_{18}O_2$, into oxy-urushic acid, $C_{14}H_{18}O_3$, which takes place by the aid of diastase in the presence of oxygen and moisture.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY,

SESSION 1882–83.

November 2nd, 1882.

Sir F. Abel, Vice-President, in the Chair.

The following papers were read:—

"On some Halogen-Compounds of Acetylene:" by Dr. R. T. Plimpton.

"On Dihydroxybenzoic Acids and Iodosalicylic Acids:" by Dr. A. K. Miller.

"On Crystalline Molecular Compounds of Naphthalene and Benzene with Antimony Trichloride:" by Watson Smith and G. W. Davis.

"Additional Evidence, by an Analysis of the Quinoline Molecule, that this Base belongs to the Aromatic Series of Organic Substances:" by Watson Smith and G. W. Davis.

"On Orcinol and some of the other Dioxytoluenes:" by R. H. C. Nevill and D. A. Winter.

"On the Varying Quantities of Malt Albuminoïds extracted by Water of Different Types:" by E. R. Moritz and A. Hartley.

"On the Derivatives of Ethylene Chlorobromide:" by J. W. James.

November 16th, 1882.

Prof. Dewar, Vice-President, in the Chair.

The following Gentlemen were elected Fellows of the Society:—

J. Ferrier, Upper Berkeley Street, W.; J. Hodgkin, Childwall, Richmond, Surrey; T. Hughes, Dudley, Worcestershire; G. Jarmay, Winnington Park, Northwich; F. Jordan, Queen's Road, Erith; W. O. Nicholson, Granville Square, W.C.; L. Reed, Croydon; H. H. Robinson, Cirencester; G. H. Sharpe, Liverpool; E. S.

Spalding, South Darenth, Kent; P. G. Stanford, Streatham; J. E. Stead, Redcar, Middlesborough.

The following papers were read:—

"Contributions to the Chemistry of Tartaric and Citric Acids:" by the late Beaumont J. Grosjean: compiled from the Author's Manuscripts, by R. Warington.

"Contributions to the Chemistry of Bast Fibres:" by C. F. Cross and E. J. Bevan.

"On the Oxidation of Cellulose:" by C. F. Cross and E. J. Bevan.

"On the Analysis of certain Vegetable Fibres:" by C. Webster.

"On the Constitution of some Bromine-derivatives of Naphthalene" (3rd notice): by R. Meldola.

"On the Constitution of Lophine:" by F. R. Japp.

December 7th, 1882.

Dr. Gilbert, President, in the Chair.

The following Gentlemen were elected Fellows:—

J. R. Cowie, Rangoon; R. Carruthers, Dumfries; R. Coulthard, Bournemouth; W. J. Chrystal, Glasgow; J. T. Bishop, Highgate, N.; E. E. Berry, Bristol; F. Bransom, Leeds; R. Blair, Hackney; E. G. Clayton, Coleman Street, E.C.; J. T. Dunn, Newcastle; H. L. Dampier, Rochester; A. G. Earl, Derby; G. Gray, Christchurch, New Zealand; A. G. Howard, Tottenham; W. A. L. Hammersley, Leek; J. L. Howe, Cleveland, Ohio; H. Hotblack, Southend; A. E. Johnson, Islington; E. Jackson, Newcastle; A. Keen, Huddersfield; J. Kilner, Bristol; J. D. McCarthy, Darlington, and Logos, W. Africa; H. C. Newton, Hampstead; S. Phillips, Hackney; R. H. Parker, 225, Oxford Street; T. F. Peppe, Arrah, Bengal; S. Rideal, Forest Hill; G. M. Taylor, Surbiton; T. E. Vasey, Leeds.

The following papers were read:—

"On the Condensation-products of Œnanthaldehyde (Part I):" by W. H. Perkin, Jun.

"On the Condensation-products of Isobutaldehyde obtained by means of Alcoholic Potash:" by W. H. Perkin, Jun.

"On a Condensation-product of Phenanthraquinone with Ethylic Aceto-Acetate:" by F. R. Japp and J. W. Streatfeild.

"On the Constitution of Lophine:" by H. E. Armstrong.

"On the Constitution of Molecular Compounds:" The Molecular Weight of Basic Ferric Sulphate:" by S. U. Pickering.

"On the Chemistry of Hay and Ensilage:" by F. W. Toms.

"On certain Brominated Carbon-compounds obtained in the Manufacture of Bromine:" by S. Dyson.

"Note on the Preparation of Diphenylene Ketone Oxide:" by W. H. Perkin.

December 21st, 1882.

Dr. Gilbert, F.R.S., President, in the Chair.

The following papers were read:—

"On the Condensation-product of Œnanthaldehyde:" by W. H. Perkin, Jun.

"On the Behaviour of the Nitrogen of Coal during Destructive Distillation, with some Observations on the Estimation of Nitrogen in Coal and Coke:" by Prof. W. Foster.

"On the Absorption of Weak Reagents by Cotton, Silk, and Wool:" by E. J. Mills and J. Takamine.

"The Alkaloïds of Nux Vomica. No. 2. On Brucine:" by W. A. Shenstone.

"Preliminary Note on Some Diazo-derivatives of Nitrobenzyl Cyanide:" by W. H. Perkin.

"Researches on the Induline Group:" by O. N. Witt and E. G. P. Thomas.

January 18th, 1883.

Dr. Gilbert, F.R.S., President, in the Chair.

The following papers were read:—

"On the Fluorine Compounds of Uranium:" by A. Smithells.

"On a New Method of Estimating the Halogens in Volatile Organic Compounds:" by R. T. Plimpton and E. E. Graves.

"On a Modified Liebig's Condenser:" by W. A. Shenstone.

"On Two New Aluminous Mineral Species; Evigtokite and Liskeardite:" by W. Flight.

"On the Volume-alterations attending the Mixture of Salt Solutions:" by W. W. J. Nicol.

February 1st, 1883.

Dr. Gilbert, President, in the Chair.

The following Gentlemen were elected Fellows:—

H. C. Bond, Bromley; G. Chandra Basu, Agricultural College, Cirencester; J. Brock, Widnes; A. M. Chance, Edgbaston; J. T. Donald, Montreal; H. C. Foote, Cleveland, Ohio; W. Fox, Trinity Square, E.C.; W. R. Flett, London International College, Spring Grove; J. A. M. Fallow, South Hampstead; E. C. Gill, Staines; F. Gothard, Burton-on-Trent; J. Hunter, Edinburgh; H. Jones, Penrith; R. B. Lee, Harwood Road, S.W.; A. H. Jackson, Manchester; Joowan Singhi, Bombay; T. Jenner, Brixton Road; J. E. Johnson, Stratford, E.; W. W. J. Nicol, Birmingham; F. W. Richardson, Bradford; Joowan Singhi, Bombay; E. S. Spencer, West Square, S.E.; C. A. Serre, Manor Road, N.; J. E. Tuit, Westminster; T. Turner, Birmingham.

The following were also elected as Honorary Foreign members:—

F. Beilstein, P. T. Cleve, H. Debray, E. Erlenmeyer, R. Fittig, H. Helmholtz, D. Mendelieff, V. Meyer, L. Meyer.

The following papers were read:—

"On some Derivatives of Fluorine:" by W. R. E. Hodgkinson and F. E. Mathews.

"On the Action of Chlorine on certain Metals:" by R. Cowper.

"Some Notes on Hydrated Ferric Oxide and its Behaviour with Sulphuretted Hydrogen:" By L. S. Wright.

"On Alpha-cyanonapthalenesulphonic Acid:" by W. R. Ditt.

February 15th, 1883.

Dr. Gilbert, F.R.S., President, in the Chair.

The following papers were read:—

"On some Derivatives of Diphenylene Ketone Oxide:" by A. G. Perkin.

"On α-Ethylvalerolactone, α-Ethyl β-Methylvalerolactone, and on a remarkable Decomposition of β-Ethyl-aceto-succinic Ether:" by S. Young.

March 1st, 1883.

Dr. Gilbert, President, in the Chair.

The following Gentlemen were elected Fellows:—

A. C. Abraham, Liverpool; G. Board, Colorado; C. N. Betts, Victoria Park; E. Bevan, Talgarth Road, W.; F. J. Cox, Warwick Road, W.; A. Collenette, Guernsey; S. Dyson, Middlesborough; W. T. Elliott, New York; H. B. Fulton, Mercia, Spain; C. G. Gren-

fell, Maidenhead; F. Halford, Cleveland Gardens, W.; W. D. Hogg, Paris; D. Hooper, Birmingham; J. J. Knight, Baltimore, U.S.; H. F. Lowe, Oxford; T. H. Leeming, Plaistow; J. E. Marsh, Rainshill, Lancashire; W. Newton, Old Kent Road, S.E.; C. Rumble, Battersea; F. Scudder, Manchester; J. O'Sullivan, Burton-on-Trent; S. A. Vasey, Leyton, Essex; T. D. Watson, Cross Street, E.C.; R. M. Walmsley, Sydenham; C. S. S. Webster, Bristol; F. Watts, Montserrat, West Indies.

The following papers were read:—

"On some Derivatives of the Isomeric $C_{10}H_{14}O$ Phenols:" by H. E. Armstrong and E. H. Rennie.

"Chemico-microscopical Researches on the Cell-contents of Certain Plants:" by A. B. Griffiths.

"On the Phenates of Amido-bases:" by R. S. Dale and C. Schorlemmer.

March 15th, 1883.

Dr. Gilbert, F.R.S., President, in the Chair.

The following papers were read:—

"On some Condensation-products of Aldehydes with Aceto-acetic Ether, and with Substituted Aceto-acetic Ethers:" by F. Matthews.

"Contributions to the Chemistry of Fairy Rings:" by Sir J. B. Lawes, Dr. J. H. Gilbert, and R. Warington.

"On Lines of no Chemical Change:" by E. J. Mills and W. M. D. Mackey.

"On Homologous Spectra:" by W. N. Hartley.

March 30th, 1883. (Annual General Meeting.) See page 224.

April 5th, 1883.

Dr. W. H. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On the Estimation of Hydrogen Sulphide and Carbonic Anhydride in Coal-gas:" by L. T. Wright.

"Contributions to the Chemistry of the Cerite Metals:" by B. Brauner.

"Some Compounds of Antimony and Bismuth containing Two Halogens:" by R. W. Atkinson.

April 19th, 1883.

Dr. W. H. Perkin, President, in the Chair.

The following Gentlemen were elected Fellows:—

T. L. Briggs, Star Chemical Works, Fulham; J. A. Basker, Bridgewater; J. B. Coleman, Nottingham; W. H. Cannon, Cullum Street, E.C.; E. C. Conrad, Well Street, E.; C. Gillet, The Brewery, Marylebone Road; E. C. Henning, Oldbury; N. K. Humphreys, Westbury, Wilts; L. Levy, Leicester.

The following papers were read:—

"On the Gases evolved during the Conversion of Grass into Hay:" by P. F. Frankland and F. Jordan.

"Note on an Apparatus for Fractional Distillation under Reduced Pressure:" by L. T. Thorne.

"On the Condition in which Carbon exists in Steel;" by Sir F. Abel and W. H. Deering.

"On the Spectrum of Beryllium, with Observations Relative to the Position of that Metal among the Elements:" by W. N. Hartley.

May 3rd, 1883.

Dr. W. H. Perkin, F.R.S., President, in the Chair.

The following papers were read:—

"On a New Oxide of Tellurium, on Tellurium Sulphoxide, and on a New Reaction of Tellurium Compounds:" by E. Divers and M. Shimosé.

"A Simple Modification of the Ordinary Method for effecting the Combustion of Volatile Liquids in Glaser's Furnace with an Open Tube:" by Watson Smith.

"On the Production of Ammonia from the Nitrogen of Minerals:" by G. Beilby.

"On the Specific Gravity of Paraffin Wax, Solid, Liquid, and in Solution:" by G. Beilby.

May 17th, 1883.

Dr. W. H. Perkin, F.R.S., President, in the Chair.

Captain W. de W. Abney, F.R.S., delivered a Lecture on "Photographic Action studied Spectroscopically."

June 7th, 1883.

Dr. W. H. Perkin, President, in the Chair.

The following papers were read:—

Laboratory Notes: (1.) "On the Action of Heat and Light on Cane and Invert Sugar." (2.) "On Hydroxylamine." (3.) "On the Recovery of Iodine from Organic Iodine-residues." (4.) "A Residual Phenomenon of the Electrolysis of Oil of Vitriol." (5.) "On an Alleged Test for Alcohol." (6.) "The Reaction of the Copper-Zinc Couple on Nitric Oxide." (7.) "On the Reducing Action of Spongy Lead:" by Dr. J. H. Gladstone and A. Tribe.

"Notes on Basic Ammonio-copper Sulphate:" by S. U. Pickering.

"Notes on Loew and Bokorny's Researches on the Probable Aldehydic Nature of Albumin:" by A. B. Griffiths.

"Note on the Action of Sulphuric Acid (sp. gr. 1·84) upon Potassium Iodide:" by Herbert Jackson.

"Action of Nitrous Anhydride on Glycerol:" by O. Masson.

June 21st, 1883.

Dr. W. H. Perkin, President, in the Chair.

The following Gentlemen were elected Fellows:—

G. S. Bowles, Kensington; C. Beringer, Garton; T. H. Coleman, Wrexham; A. Esilman, Manchester; H. E. Harrison, Great Ormond Street; C. Hulke, Deal; H. Heap, Hereford; B. Hobbs, Maidenhead; C. T. Heycock, Cambridge; W. J. Livingstone, Stepney; B. P. Lascelles, Oxford; H. R. Mill, Edinburgh; M. T. Purcell, Dublin; J. E. Richardson, Carthagena; F. G. Roberts, Upper Clapton; W. R. Reffell, Peckham; A. Smith, Verulam Club; E. H. B. Stephenson, Clapham; A. W. Toward, Fleet Street; A. H. Samuel, Liverpool; D. Wilson, Glasgow; R. Williams, Manchester.

The following papers were read:—

"On Evaporation in Vacuo:" by Prof. H. McLeod.

"On the Preparation of Pentathionates:" by S. Shaw.

"Note on Hydrocarbons from Camphor:" by Dr. H. E. Armstrong.

"On the Rate of Decomposition of Ammonium Nitrate:" by H. Veley.

"On a New Gas-burner for Heating Gas-tubes:" by Prof. Ramsay.

"Note on the Action of Allylic Iodide upon Phenol in Presence of Zinc or Aluminium-foil:" by P. F. Frankland and T. Turner.

"On a Bye-product of the Manufacture of Aurin:" by A. Claparède and Watson Smith.

Donations to the Library, 1882–83:—

"A Treatise on the Distillation of Coal-tar and Ammoniacal Liquor:" by G. Lunge: from the Publisher.

"The Wave-lengths of the Principal Frauenhofer Lines of the Solar Spectrum:" by Dr. T. C. Mendenhall: from the Author.

"The Minerals of New South Wales:" by A. Liversidge: from the Author.

"Annual Report of the Department of Mines, New South Wales:" by A. Liversidge: from the Author.

"New South Wales in 1881:" compiled and edited by Thomas Richards: from the Royal Society of New South Wales.

"Reports on Gunpowders:" by F. W. Toms: from the Author.

"The Comparative Effects of Two Metameric Bodies on the Growth of *Nicotiana longiflora*:" by J. Emerson Reynolds: from the Author.

"Madeira Spectroscopic," being a Revision of 21 places in the Red Half of the Visible Solar Spectrum with a Rutherford Diffraction Grating: by C. Piazzi Smyth: from the Author.

"Metals: their Properties and Treatment:" by C. L. Bloxam and A. K. V. Huntington: from the Authors.

"The Organic Constituents of Plants and Vegetable Substances, and their Chemical Analysis:" by C. G. Wittstein; translated, with additions, by F. Baron von Müller: from the Translator.

"The Conservation of Solar Energy: a Collection of Papers and Discussions:" by C. W. Siemens: from the Author.

"Inorganic Chemistry:" by H. Watts: from the Publishers.

"Ueber Condensationen einiger Aldehyde mit Acetessigäther und substituirten Acetessigäthern:" von. F. E. Matthews: from the Author.

"Ueber einige Homologe des Resorcins:" von E. Knecht: from the Author.

"Die Atomgewichte der Elemente:" von Lothar Meyer and K. Seubert: from the Authors.

"Researches on the Complex Inorganic Acids:" by Wolcott Gibbs: from the Author.

"Compte rendu des Travaux du Laboratoire de Carlsberg, 1878—1883:" from the University.

"Memoirs of the Science Department of the University of Tôkiô:"

"The Wave-lengths of the Principal Frauenhofer Lines of the Solar Spectrum:" by T. C. Mendenhall:

"The Chemistry of Saké Brewing:" by R. W. Atkinson:

"Report of the Meteorology of Tôkiô:" by T. C. Mendenhall:

from the University.

"Journal of the Royal Society of New South Wales," 1881. Vol. xvi: from Prof. Liversidge.

"The Ephemeris of Materia Medica, &c.," Nov. 1882:

from the Editor.

"Reports of the Medical Officer of the Privy Council and Local Government Board for 1874, 1879—80, 1880—1881:"

from Dr. G. Buchanan.

"Proceedings of the American Academy of Arts and Sciences." New Series. Vol. ix. 1882: from the Academy.

"Calendar of the Pharmaceutical Society for 1882:"

from the Society.

"Memorie dell' Accademia delle Scienze di Bologna." Serie 4, Tomo ii: from the Academy.

"Army Medical Department Report for 1880:"

from the Department.

"Proceedings of the Academy of Natural Sciences at Philadelphia, 1857—1862:" from the Academy.

"Wissenschaftliche Beigaben zum Program der St. Galler Kantonschule:" von Dr. Joseph Adolf Kaiser: from the Author.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften in Wien:" Bde. 42, 43.

"Sitzungsberichte derselben:" lxxxiii, Heft 5; lxxxiv u. lxxxv, 1 und 2 Hefte, 1881—82: from the Academy.

"Journal of the Iron and Steel Institute," 1882, No. 1, and 1879, No. 1: from the Institute.

"Journal of the Royal Society of New South Wales," 1881, vol. xvi: from Prof. Liversidge.

"Journal of the Iron and Steel Institute," 1882. Vol. ii:

from the Institute.

"Scientific Transactions of the Royal Dublin Society." Series ii. Vols. i and ii, 1882: from the Society.

"Nova Acta Academiæ Cæsareæ Leopoldino-Carolinæ Germanicæ Naturæ Curiosorum." Tomus xliii, cum Tabulis xxviii:

from the Academy.

"Annals of the New York Academy of Sciences." March and May, 1882.

"Transactions" of the same. November and December, 1881, and January and February, 1882: from the Academy.

"Denkschriften der Kaiserlich-Königlichen Akademie der Wissenschaften." Bde. xliii, xliv, 1882: from the Academy.

The following have been presented by Dr. A. W. Hofmann:—

"Physikalisch-chemische Notizen:" von J. J. Pohl.

"On the Temperature of the Earth and Sea in Reference to the Theory of Central Heat:" by Alfred S. Taylor.

"On the Rotation of Hollow Spheres of Metal by Heat:" by G. Gore.

"Recherches sur les Quantités de Chaleur degagées dans les Actions Chimiques et Moléculaires:" par P. A. Favre et J. T. Silbermann.

"Ueber die Temperatur der aus kochenden Salzlösungen und gemischten Flüssigkeiten entweichenden Dämpfe:" von G. Magnus.

"Uebersicht der Resultate einiger Arbeiten welche Regelmässigkeiten in den Specifischen Gewichten und den Siedepunkten der Chemischen Verbindungen behandeln:" von Hermann Kopp.

"Some Experiments on Sonorous Flames, with Remarks on the Primary Source of their Vibration:" by W. B. Rogers.

"Force Crystallogénique:" par F. Kuhlmann.

"On the Absorption of Gases by Charcoal:" by John Hunter.

"Sul Coefficiente di Compressibilità dell Acqua per mezzo dell' Apparato detto di Oersted, e sul piu vero e men recente Autore dell' Apparato medesimo. Cenni di alcune modificazione alla vecchià Scienza:" del Professore G. Gherardi.

"Ueber den Einfluss der Atomistischen Zusammensetzung C-, H-, und O-haltiger flüssiger Verbindungen auf die Fortpflanzung des Lichts:" von H. Landolt.

"Researches on the Method of Preserving the Sensitiveness of Collodion Plates:" by J. Spiller and W. Crookes.

"On a Method of Increasing Certain Effects of Induced Electricity:" by W. R. Grove.

"Ueber nicht polarisirbare Elektroden:" von E. Dubois-Reymond.

"Untersuchungen über Thierische Electricität:" von Emil Dubois-Reymond.

"The Relation between the Atomic Weights of the Chemical Elements:" by J. P. Cooke. January, 1854.

"On the Theory of Types in Chemistry:" by T. Sterry Hunt.

"On the Properties of Water and Ice:" by Otto Pettersson.

"Expériences sur quelques Métaux et quelques Gaz:" par Despretz. 4to, 1858.

"De la Migration du Phosphore dans la Nature:" par B. Corenwinder.

"Bemerkungen über Jacquelain's Aequivalentbestimmung des Phosphors:" von A. Schrötter.

"Composition and Phosphorescence of Plate-sulphate of Potash:" by F. Penny.

"Sur une Combinaison de Bioxide de Chrome et de Dichromate Potassique:—Dichromate Kalichromique, $(CrO_2)_3(CrO_3)_2K_2O,H_2O$:" par D. Tommasi.

"Sur la Dilatation des Aluns:" par W. Spring.

"Beiträge zur Chemie der Platinmetalle:" von Carl Claus.

"On some Phosphides of Iridium and Platinum:" by F. W. Clarke and O. T. Joslin.

"Ueber die Cyanverbindungen der Platinmetalle:" von C. A. Martius.

"Contributions to Chemical Mineralogy:" by James D. Dana.

"Notes on the Economic Mineralogy of Nova Scotia:" by Prof. How.

"Ueber die Processe der Vulkanischen Gesteine Islands:" von R. Bunsen.

"On the Phosphoric Strata of the Chalk Formation:" by J. M. Paine and J. T. Way.

"Memoirs of the Geological Survey of Great Britain and of the Museum of Practical Geology.—The Iron Ores of South Staffordshire."

"Recherches sur les Verres provenant de la Fusion des Roches:" par A. Delesse.

"On the Phosphoric Strata of the Chalk Formation:" by J. M. Paine and J. T. Way.

"Recherches sur le Porphyre Quartzifère:" par A. Delesse.

"Examination into the Comparative Qualities and Fitness for Building Purposes of Samples of Stone from Various Localities in the Island of Portland:" by F. A. Abel.

"The Noteworthy Springs and Spas of Norfolk:" by H. B. Woodward.

"Chemical Examination of certain Lakes and Springs on the Turko-Persian Frontier, near Mount Ararat:" by H. M. Witt.

"Report on the Sulphur Springs of Harrogate for the years 1841 and 1842."

"On the Conservancy of Rivers, Prevention of Floods, Drainage, and Water Supply:" by J. M. Blake.

"Report to the Metropolitan Board of Works on the Main Drainage of the Metropolis." 4to. 1858.

"Report of the Honourable Commissioners of Sewers of the City

of London, on Sewage and Sewer Gases, and on the Ventilation of Sewers:" by Henry Letheby.

"The Water-supply of the City of New York:" by E. Waller.

"Recherches sur les Affinités: De la Formation et de la Décomposition des Ethers:" par MM. Berthelot et Péan de St. Gilles.

"On a New Reaction for the Production of Anhydrides and Ethers:" by John Broughton.

"Recherches sur les Combinaisons des Acides Borique et Silicique avec les Éthers:" par M. Ebelmen.

"Mémoire sur de nouvelles Combinaisons de l'Acide Borique avec les Éthers:" par M. Ebelmen.

"L'action du Brome sur l'Iodure d'Aldehydène (Ethylidène): par Maxwell Simpson.

"On some of the Constituents of the Tar obtained by the Destructive Distillation of Brown Coal:" by Max Durre.

"On the Bases produced by the Destructive Distillation of Peat:" by A. H. Church and E. Owen.

"Note sur les Sels Organiques du Thallium:" par F. Kuhlmann.

"Combinaisons de la Glycérine avec les Acides, et Reproduction artificielle des Corps gras neutres:" par M. Berthelot.

"Ueber die Isomérie der Fumarsäure und Maleinsäure, sowie der Itaconsäure, Citraconsäure, und Mesaconsäure:" von Hermann Kolbe.

"Vorläufige Notiz über Olivenöl:" von W. Heintz.

"On the Optical Properties of a Newly Discovered Salt of Quinine [1852]:" by W. B. Herapath.

"Zur Kenntniss einiger isomeren Bromnitrobenzoylsulfonsäuren und ihrer Reduktionsproduckte:" von Launcelot W. Andrews.

"Ueber Triphenylborat, nebst einem Anhang über ein neues Luftthermometer:" von Launcelot W. Andrews.

"On Organic Substances Artificially formed from Albumin:" by A. H. Smee.

"Recherches Chimiques sur la Réspiration des Animaux des diverses Classes:" par V. Regnault et J. Reiset.

"Observations on some of the Products of the Putrefaction of Vegetable and Animal Substances, and their Relations to Pathology:" by W. K. Salleran.

"Recherches sur l'Assimilation du Carbone par les Feuilles des Végétaux:" par B. Corenwinder.

"Mémoire sur la Structure et la Composition chimique de la Canne-à-Sucre:" by M. Payen.

"Recherches sur la Garance d'Alsace:" par E. Kopp.

"Nouveau Procédé pour la Culture de la Vigne:" by J. Persoz.

"On Artificial Manures:" by Justus Liebig.

"On the Composition and Money-value of Different Varieties of Guano:" by J. T. Way.

"Dosage de l'Arsenic dans les Métaux et dans leurs Alliages à l'aide d'une nouvelle méthode:" par J. Levol.

"Beiträge zur Analyse der Pflanzenaschen:" von H. Wackenroder.

"On the Valuation of Soils and the Nutrition of Plants:" by Robert Galloway.

"On Spectrum Analysis:" by William Allen Müller.

"Silicatisation, ou Application des Silicates Alcalins Solubles au Durcissement des Pierres, des Ciments et des Plâtrages, à la Peinture, à l'Impression, aux Apprêts, &c.:" by F. Kuhlmann.

"Rapport sur les Arts Céramiques:" par feu M. Ebelmen et M. Salvétat.

"On Mineral Candles and other Products manufactured at Belmont and Sherwood:" by the Rev. John Barlow.

"Mémoires sur la Composition et l'Emploi des Gaz provenant des Opérations Métallurgiques et des Gaz produits au moyen de divers Combustibles:" par M. Ebelmen.

"Explosions in Coal-mines, their Causes, and the Means available for their Prevention or Control:" by J. Kenyon Blackwell.

"Contributions to the Metallurgy of Copper:" by A. Dick.

"The Iron Ores of South Staffordshire" (Memoirs of the Geological Survey of Great Britain).

"On the Chemical Changes which Pig Iron undergoes during its Conversion into Wrought Iron:" by F. C. Calvert and R. Johnson.

"Paper on Cotton, Flax, &c., and their Bleaching:" by F. C. Calvert.

"Natur und Wesen der Gerberei des Leders:" von. F. Knapp.

"On the Security and Manufacture of Bank Notes." 4to. 1856: by H. Bradbury.

"Examen des Matières artificielles derivées du Goudron de Houille." 4to. 1861: par E. Kopp.

"Beiträge zur genaueren Kenntniss der Chemischen Constitution des Weines:" von F. L. Winckler.

"On the Acidity, Sweetness, and Strength of different Wines:" by H. Bence Jones.

The following have been presented by the University of Christiania:—

"Om Druesukkerets Fremstelling efter Neubauer's Forskrift ved Hyælp af Schwarz's Methode, og dets Renhet:" af Prof. Worm Müller.

"Om Druesukkerets Fremstelling og Titrering med Knapp's Vædske:" af Jac. G. Otto.

"Om Kreatininets Forhold til Kobberoxyd og Alkali:" af Prof. Worm Müller.

"Om Urinsyrens Forhold til Kobberoxyd og Alkali:" af Prof. Worm Müller.

"Om Spektrophotometriske Konstanters Variation:" af Jac. G. Otto.

"Om Bromkalium i Diabetes Mellitus:" af J. Worm Müller.

"Om Oxyhæmoglobin af Svineblod:" af Jac. G. Otto.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS. 1883.

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ERRATA IN VOL. XLIII.

Page.	Line.	
234	3 from top	*for* 840 *read* 760.
316	2 „ bottom	*for* "investigators" *read* "investigations."
391	4 „ top	*for* "chemical kinetic energy" *read* "chemical activity, or in other words greater kinetic energy."
—	13 „ „	*for* "Johnston" *read* "Johnstone."
—	15 „ „	*for* "faradic" *read* "periodic."
396	3 „ bottom	*for* "1 + and K" *read* "H and K."
398	13 „ „	*for* "these facts" *read* "the facts."
399	4 „ top	

for

Copper. wave-lengths.	Tellurium. wave-lengths.
3307·4	3307·5
3290·2	3290·0
3280·5	3280·4 (very strong)
3273·6 (very strong)	3273·8 (very strong)
3264·3	3264·4
3247·3 (very strong)	3247·2 (very strong)

read

Copper. Wave-lengths.	Tellurium. Wave-lengths.
3307·0	3307·1
3289·8	3289·6
3280·1	3280·0 (very strong)
3273·2 (very strong)	3273·4 (very strong)
3263·9	3264·0
3246·9 (very strong)	3246·8 (very strong)

399	24 from top	*for* "silica" *read* "silicon."
411	4 „ bottom	*for* "23·7" *read* "33·7."
421	3 „ top	*for* $\frac{1}{1}$ *read* $\frac{1}{2}$.
429	9 „ „	*after* "amido-group" *insert* "when the *para*-position is open."
436	3 „ bottom	(in footnote) *for* "diazo-" *read* "disazo."

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